# SAMPLING AND ANALYSIS OF NEW BRUNSWICK MANGANESE DEPOSITS

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# SAMPLING AND ANALYSIS OF NEW BRUNSWICK MANGANESE DEPOSITS

## INTRODUCTION

This report describes the work done on the North Hartford and Plymouth manganese deposits located in the Woodstock area, New Brunswick. Atlantic Analytical Services in Saint John was the prime contractor and manager of the project. The major objectives of this work included trenching of the manganese deposits and carrying out comprehensive mineralogical and chemical analyses on eight bulk samples taken in such a way as to be representative of the sampled sections of the manganese deposits. In order to effectively meet the requirements of this project, the work was broken down into the following three subgroups: A.) Trenching and Sampling; B.) Mineralogical Analysis; C.) Chemical Analysis.

Part A.) was subcontracted to Mr. W. Gates, Geologist; formerly chief geologist with Heath Steele Mines. He was responsible for trenching, collecting, packaging and shipping of the samples.

Part B.) was subcontracted to Research and Productivity Council (RPC) in Fredericton, New Brunswick. Their task was to carry out exhaustive mineralogical studies of the samples and identify the various mineral phases which contain the elements of interest in addition to preparing the samples.

...../ii

Part C involved performing comprehensive quantitative analyses of 16 specified chemical elements on the samples and was carried out by Atlantic Analytical Services Ltd.

## PART A: TRENCHING AND SAMPLING OF NEW BRUNSWICK MANGANESE DEPOSITS

### INTRODUCTION

Over the period January 12 to January 22, trenching for manganese samples was carried out on the North Hartford and Plymouth deposits in the Woodstock Area, New Brunswick.

Sample sites were outlined by N. B. government geologists, Timm Webb and Dean Thibault. Samples were taken by back hoe trenches to a depth of three feet. Considerable effort and expense was necessary to remove snow for accessibility to sample sites.

Eight manganese samples were obtained, each of 200 Kg. Three were obtained from the North Hartford deposit and five from the Plymouth deposit. Eight trenches three from North Hartford and five from Plymouth were excavated, each trench 400' in length. Heavy snow fall hindered easy access to the area and complicated trenching. Otherwise the project went along very well.

Costs on the whole were less than projected. However a heavy snow fall necessitated the use of a large bulldozer which involved an additional expenditure of $4,071.00.

Cummings Construction of Upper Woodstock carried out the field work and performed well.

Chronological Record

Gates - Woodstock Mn

Preparation pre start up - travelled to Millville to discuss with Robert Connor the logistics of the project and the equipment required. Connor and I then drove to Nackawik and arranged for purchase of eight (8) 45 gallon drums for manganeses samples. In the same village, Mr. Edison Cummings agreed to do the actual trenching. We then proceeded to Woodstock to ascertain depth of snow and locate suitable motel. Returned to Millville, then to Newcastle.

Sunday - January 12

Travelled to Woodstock arriving in the evening in preparation for start of project Monday morning.

Monday - January 13

The Hartford and Plymouth sample sites were examined with two government geologists - Timm Webb and Dean Thibault. Edison Cummings, former contractor, was unable to carry out the project, due to an accident with his backhoe and recommended Cummings Construction. In company with government geologists, we discussed prices and capabilities with the new contractor, Eric Cummings. He advised us that because of the heavy snow-fall it would be necessary to bulldoze roads and trenching areas for backhoe access. I decided that Cummings Construction were suitable for the project based on apparent competence, availability of equipment, and knowledge of the area.

Tuesday - January 14

Landowners of the trenching areas were contacted for permission to trench. Hugh Tompkins - Hartford deposit and H. Haines- Plymouth, both gave their consent.

A road into North Hartford deposit was "opened up" and one trench area was uncovered.

Wednesday - January 15

Continued to remove snow and commenced trenching on the North Hartford deposit.

Thursday - Friday- January 16-17

Completed trenching and snow removal on the North Hartford deposit.

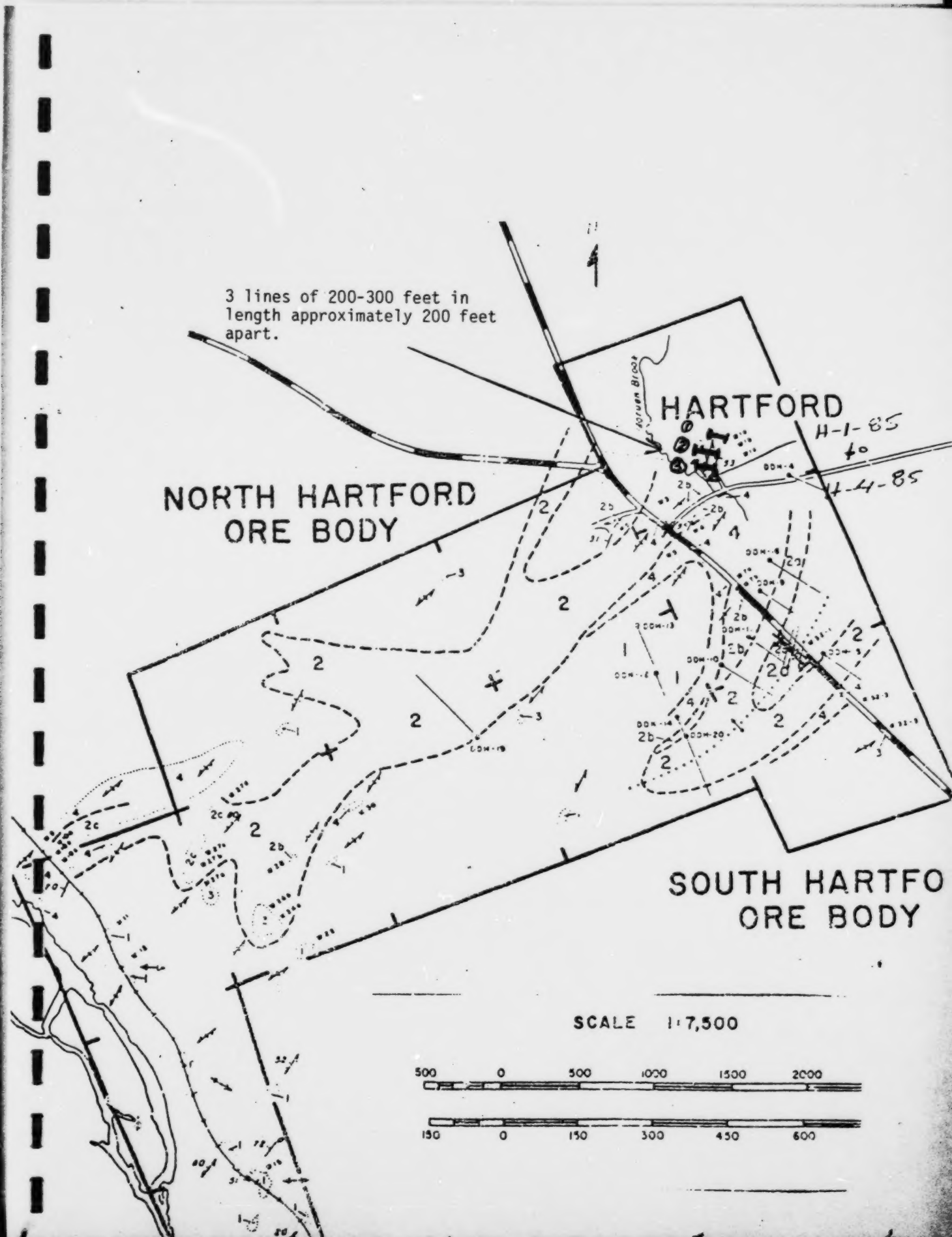
Sunday - January 19

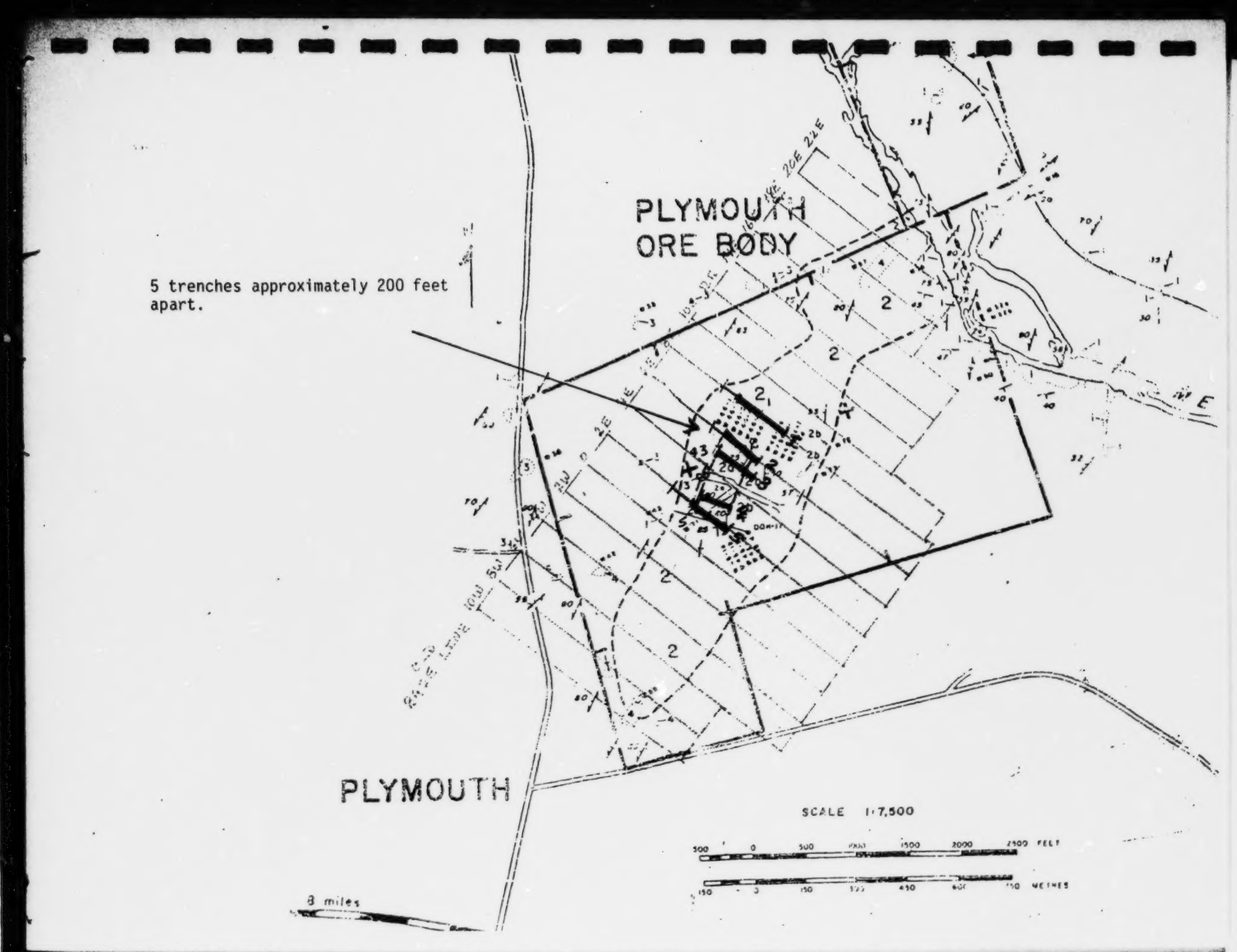
Travelled to Woodstock to commence trenching on Plymouth deposit. This was completed on the evening of January 22 and I returned to Newcastle on January 23.

## EXPENDITURES

| | | |
|---|---|---|
| Bulldozer-snow removal | $4,071.00 | |
| ripping | 262.50 | |
| 1/2 ton truck | 105.00 | |
| *Purchase drums and transport samples to Fredericton R.P.C. | 381.00 | |
| Trenching | 2,047.50 | $6,867.00 |
| Gates - consulting | | |
| January 12 - 10 days at $200.00 | $2,000.00 | |
| Expenses - Motel | 224.33 | |
| | 175.85 | |
| Travel - mileage | | |
| 680 x 0.32/mile | 217.60 | |
| Preparation - mileage and expenses | 105.00 | |
| | | $2,722.78 |
| Misc. - S.M.T. | 3.50 | |
| Xerox copies | 4.00 | |
| Other meals | 4.44 | |
| Tips-meals $77.35 x 15% | 11.60 | |
| | | $ 23.54 |
| | | $9,613.32 |

*Boom truck plus $200.00 for transport to Fredericton - R.P.C.


3 lines of 200-300 feet in
length approximately 200 feet
apart.
HARTFORD
H-1-85
to
H-4-85
NORTH HARTFORD
ORE BODY
SOUTH HARTFO
ORE BODY
SCALE 1:7,500
500 0 500 1000 1500 2000
150 0 150 300 450 600


5 trenches approximately 200 feet apart.
PLYMOUTH ORE BODY
PLYMOUTH
SCALE 1:7,500
500 0 500 1000 1500 2000 2500 FEET
150 0 150 300 450 600 750 METRES
8 miles

# MINERALOGY OF THE PLYMOUTH AND NORTH HARTFORD MANGANESE DEPOSITS NEAR WOODSTOCK, N.B.

for

Atlantic Analytical Services Limited
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Mineralogist

REPORT NUMBER: MDP/86/01
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JM/mb/REP1

TABLE OF CONTENTS


| | | Page |
|---|---|---|
| 1.0 | SUMMARY | 1 |
| 2.0 | INTRODUCTION | 2 |
| 3.0 | ANALYTICAL METHODS | 3 |
| | 3.1 Sample Preparation | 3 |
| | 3.2 Sample Examination | 3 |
| 4.0 | RESULTS | 8 |
| | 4.1 General Mineralogy of the Plymouth Ore Samples | 8 |
| | 4.1.1 Plymouth 1 | 8 |
| | 4.1.2 Plymouth 2 | 17 |
| | 4.1.3 Plymouth 3 | 29 |
| | 4.1.4 Plymouth 4 | 38 |
| | 4.2 General Mineralogy of the North Hartford Ore Samples | 48 |
| | 4.2.1 North Hartford 1 | 48 |
| | 4.2.2 North Hartford 2 | 59 |
| | 4.2.3 North Hartford 3 | 70 |
| 5.0 | CONCLUSIONS | 80 |
| 6.0 | RECOMMENDATIONS | 82 |
| APPENDIX A-1 | | |
| APPENDIX A-2 | | |

# LIST OF FIGURES


| | | Page |
|---|---|---|
| Figure 1. | Enlarged image of the NH1 polished thin section taken with the copy camera. | 4 |
| Figure 2. | Red slate and carbonate containing acicular to massive hematite (H). | 10 |
| Figure 3. | Hematite-rich red slate with rhodochrosite. | 15 |
| Figure 4. | Thin manganite (M) and minor jacobsite (J) veins in silicified slate. | 18 |
| Figure 5. | Red slate containing Fe/Ti oxides. | 19 |
| Figure 6. | Spherulitic to massive braunite... | 21 |
| Figure 7. | Irregular hematite (H) with small braunite (B) blebs intergrown psilomelane (Ps) and very minor pyrolusite... | 26 |
| Figure 8. | Spongy blebs of Mn(K)Al Silicate (A)... | 28 |
| Figure 9. | Red slate with Fe/Ti oxides. | 30 |
| Figure 10. | Massive hausmannite (H) with psilomelane (Ps) rims and minor pyrolusite (P)... | 36 |
| Figure 11. | Silicified green chloritic slate of finely intergrown K(Fe) mica (P), slightly lighter Fe(Mn) chlorite (Ch), quartz (Q), and alkali feldspar. | 37 |
| Figure 12. | Cryptocrystalline manganese-rich siderite(S). | 40 |

LIST OF FIGURES (Cont'd)


| | | Page |
|---|---|---|
| Figure 13. | Hematite (H)-rich dark grey/red slate with finely intergrown rhodochrosite (with minor calcium) and MnCa silicate (Rh). | 41 |
| Figure 14. | Intergrown psilomelane (Ps) and hausmannite (H) with quartz, K feldspar, and minor rhodochrosite (Ca). | 46 |
| Figure 15. | Silicified green chloritic slate with bright framboidal pyrite (F) and minor apatite (A). | 49 |
| Figure 16. | Green chloritic slate containing bright rhodochrosite (R) and platey FeK(Mg) mica (Ph). | 50 |
| Figure 17. | Light brown/orange slate... | 52 |
| Figure 18. | Yellow/green chloritic slate with minor pyrophanite (P) and Ti oxide (T). | 53 |
| Figure 19. | Layered manganite (M) and hausmannite (H) pseudomorph after braunite. | 55 |
| Figure 20. | Silicified light brown/green slate with a large manganite/pyrolusite "vein" (V1). | 62 |
| Figure 21. | A fragment of manganese oxide-rich silicified slatey material containing a large psilomelane/minor pyrolusite vein (V1)... | 63 |
| Figure 22. | Manganese oxide-rich slatey material with a large blocky psilomelane vein (V1). | 68 |
| Figure 23. | Manganite-rich slate with dark interstitial quartz, albite, and FeMnK mica. | 76 |

LIST OF FIGURES (Cont'd)


| | | Page |
|---|---|---|
| Figure 24. | Red slate with irregular grains of hematite (H) and psilomelane (P). | 77 |
| Figure 25. | Dark grey silicified slatey material with fine elongate hematite (H)... | 79 |

# LIST OF TABLES


| | | Page |
|---|---|---|
| Table 1 | Weights of Crushed Manganese Ore Samples | 5 |
| Table 2 | Distribution and Brief Description of Fragment Types in Sample P1 | 11 |
| Table 3 | Manganese-Bearing Phases in Plymouth 1 Sample | 14 |
| Table 4 | Distribution and Brief Description of Fragment Types in Sample P2 | 22 |
| Table 5 | Manganese-Bearing Phases in Plymouth 2 Sample | 24 |
| Table 6 | Distribution and Brief Description of Fragment Types in Sample P3 | 31 |
| Table 7 | Manganese-Bearing Phases in Plymouth 3 Sample | 34 |
| Table 8 | Distribution and Brief Description of Fragment Types in Sample P4 | 42 |
| Table 9 | Manganese-Bearing Phases in Plymouth 4 Sample | 44 |
| Table 10 | Distribution and Brief Description of Fragment Types in Sample NH1 | 56 |
| Table 11 | Manganese-Bearing Phases in North Hartford 1 Sample | 58 |
| Table 12 | Distribution and Brief Description of Fragment Types in Sample NH2 | 64 |

LIST OF TABLES (Cont'd)


| | | Page |
|---|---|---|
| Table 13 | Manganese-Bearing Phases in North Hartford 2 | 66 |
| Table 14 | Distribution and Brief Description of Fragment Types in Sample NH3 | 72 |
| Table 15 | Manganese-Bearing Phases in North Hartford 3 | 74 |
| Table 16 | A summary of the Major and Common Minerals for Samples Studied | 81 |

## 1.0 SUMMARY

A mineralogical study of eight samples from the Plymouth and North Hartford manganese-rich deposits near Woodstock, N. B. was undertaken. The samples were crushed and homogenized in preparation for examination using optical and SEM/EDS (Scanning Electron Microscope with an Energy Dispersive System) techniques. The dominant manganese-bearing phases were found to be manganese-rich carbonates, manganiferous chlorites, braunite, manganite, psilomelane, pyrolusite, hausmannite, jacobsite, pyrophanite, Mn(K)Al silicate, and various manganiferous micas. Note that the manganese often occurs as small amounts in rock forming minerals such as chlorite and the various micas. These manganese-bearing phases are generally finely intergrown with other minerals, their longest dimensions not exceeding approximately 50 micron and often being less than 25 micron. This fine-grained nature and the great variety of mineral types involved make physical separation as a method of liberating the manganese minerals very difficult. The fact that much of the manganese is present in phases from which it is not easily recoverable, also creates problems for the chemical separation methods. A better understanding of these two deposits, especially the positions and extent of the various manganese-bearing phases would greatly aid in the processing problem, as well as recovery.

## 2.0 INTRODUCTION

In November 1985, Atlantic Analytical Services Limited requested that the Department of Mineral Processing and Development of the Research and Productivity Council prepare a cost estimate for mineralogical studies necessary for a process assessment of manganese deposits as required by the Department of Supply and Services (DSS) request for proposal entitled "Sampling and Analysis of New Brunswick Manganese Deposits" (DSS File No. 07SQ.23440-5-9216). The DSS statement of work is given in Appendix A-1. The cost for detailed mineralogical assessment were given to Atlantic Analytical in a letter dated November 13, 1986 (Appendix A-1). The costs allowed in the contract precluded a detail assessment. Therefore, Atlantic Analytical on behalf of DSS requested that only a mineralogical and petrographic description be prepared for each sample.

Eight samples, five from Plymouth and three from North Hartford, were collected in January and submitted to RPC on January 23, 1986. The samples were crushed and homogenized. A mineralogical study was undertaken to determine the nature of the manganese phases present. A general description of each sample, a very general estimate of the distribution of manganese phases in each sample, and a brief description of the more common of these phases are included in this report.

## 3.0 ANALYTICAL METHOD

### 3.0.1 Sample Preparation

Eight Mn-ore samples were submitted to RPC on January 23rd, 1986. Of the eight, six contained a substantial amount of mud and soil (some even contained fine roots). Samples P1, P2, P3, P4, P5 and NH3 were coarsely sieved to remove a large portion of this material. The "clean" fractions were crushed to approximately half inch size using a large and then a small jaw crusher. The crushed ore was put in barrels which were sealed and then rolled for 3-4 hours each to homogenize the material. Table 1 lists the final weight of each sample.

Approximately 2 kilograms of each ore sample were removed and crushed to -18 mesh (<1.00 mm) using a cone crusher and a rolls crusher. A portion of this was sent to Atlantic Analytical for chemical analysis. The fine component (-25 mesh, <710 microns) in the remaining material was removed. One polished thin section per sample was prepared for optical examination using the -18 +25 mesh (<100 mm, >710 microns) portion.

Photographs of the thin sections were taken using a copy camera. These were enlarged to approximately 6 1/2 times the size of the thin sections (see Figure 1). These images were very useful in finding and identifying specific fragments during the sample examination.

### 3.0.2 Sample Examination

Each sample has been examined optically. A minimum of 95 grains per sample have been classified using a combination of general colours, textures and mineral assemblages as criteria (see Appendix A-2 for details). Due to the very fine-grained nature of

Figure 1. Enlarged image of the NH1 polished thin section taken with the copy camera. Notice the variation in areal fragment size (Image is 6 1/2 times original).

TABLE 1 Weights of Crushed Manganese Ore Samples

| Sample | Weight* | Substantial Mud? |
|---|---|---|
| P1 | 111 kg | Yes |
| P2 | 196.5 | Yes |
| P3 | 149 | Yes |
| P4 | 226 | Yes |
| P5 | 166 | Yes |
| NH1 | 234 | No |
| NH2 | 265 | No |
| NH3 | 211 | Yes |

* The weight of the empty barrels is approximately 15 kilograms and has been subtracted from the weights measured to arrive at this figure.

much of the ore, the classifications often relied on the general colour and/or texture rather than the more definite identification of mineral assemblages. A number of grains (from 15 to 30 per sample), either typical of a classification or containing an unusual component, were examined qualitatively using an SEM/EDS (Scanning Electron Microscope with an Energy Dispersive System) to identify fine-grained to cryptocrystalline assemblages and confirm previous optical identification of coarser phases.

A very general estimate of the distribution of Mn-bearing phases in each sample has been devised by considering the distribution of Mn-minerals in each fragment type and then the distribution of the fragment types in the sample population. The estimated distributions are very general because:

(a) all estimates of mineral content are visual and, due to the fine-grained nature of the material, often rely on SEM/EDS back-scatter images, and

(b) the distributions of fragment types are calculated assuming the surface area of each fragment is equal (see Figure 1 for example of variation actually present).

Minerals are often listed with bracketed elements following them, for example rhodochrosite (Ca). This means that the element, calcium in this case, is present in minor amounts in the mineral as indicated qualitatively by SEM/EDS analysis.

Also in many of the brief descriptions of fragment types oxides are listed with slashes between the accompanying elements, for example Fe/Mn/Ti oxides. This indicates a series of oxides containing any combination of these elements, in this case perhaps ilmenite (FeTi oxide), hematite (Fe oxide), and pyrophanite (Mn Ti oxide).

Many of the cryptocrystalline minerals could not be positively identified because identification relied solely on SEM/EDS technique and only qualitative data was collected using this technique. However, where optical properties could be seen, the minerals were more definitely identified.

Sample NH5 was examined optically and no significant amounts of manganese-bearing phases were observed. Thus, this sample was not studied in any more detail.

In various places in the report the term "gel" is used. This refers to a dark brown material in which the individual minerals are too fine to identify. It is probably a chemical precipitate. Pseudomorphs of "gel" are also referred to. In these cases the "gel" has taken on an euhedral crystal form.

# 4.0 RESULTS

## 4.1 General Mineralogy of the Plymouth Ore Samples

Although relative abundances vary, the most common types of manganese phases present are basically the same throughout the Plymouth samples. All contain a significant amount of manganese-rich carbonate, manganiferous chlorite, manganite, psilomelane, and hausmannite or pyrolusite (both in P3). Samples P1 and P2 contain relatively large amounts of braunite. P2 also contains significant amounts of Mn(K)Al silicate. The occurances of these minerals vary from sample to sample. The following sections describe these occurances and the general nature of the samples in some detail.

### 4.1.1 Plymouth 1

The sample population from the Plymouth 1 crushed ore contains 18 fragment types. The predominant types are:

(a) red slate containing minor manganoilmenite, ilmenite, Fe(Ti) oxide, often secondary manganese oxides, and secondary rhodochrosite/rhodonite blebs.

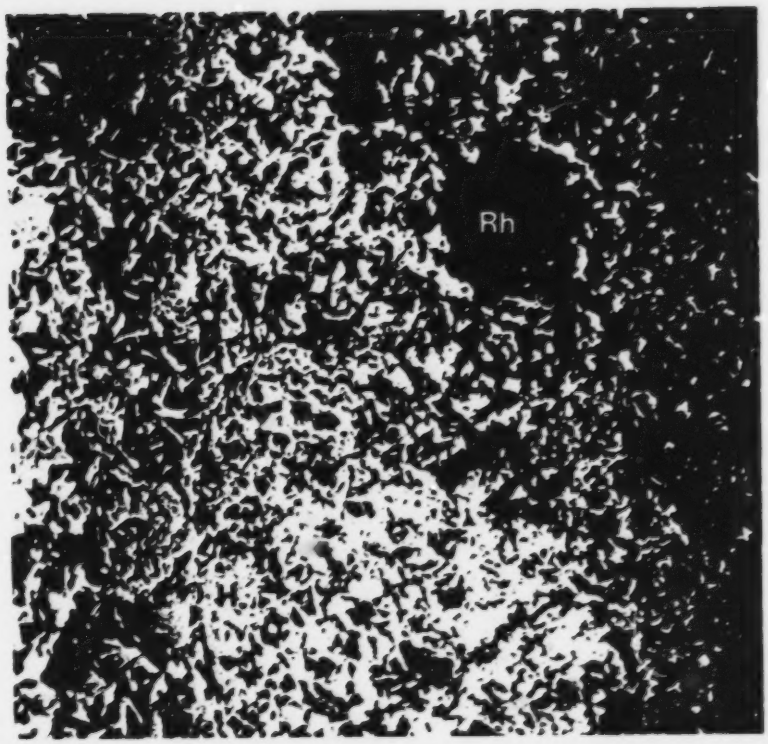
(b) red slate and carbonate containing acicular to massive (matted) hematite and often secondary manganese oxides (see Figure 2).

(c) fine to medium grained calcite with varying amounts (10-55% of other phases such as quartz, chlorite, white mica and alkali feldspar.

(d) green slate containing large quartz and albite lenses; dark brown "gel" pseudomorphs; and minor ilmenite, hematite and Fe oxide.

(e) cryptocrystalline (often spherulitic) or coarse-grained rhodochrosite commonly with quartz, chlorite, white mica, and rhodonite of varying amounts.

These types make up approximately 75% of the sample. The remaining fragments are comprised of various types of slates (metamorphosed arkose?), coarse- (to medium-) grained quartz, massive secondary manganese oxides and massive braunite (see Table 2 for distribution and brief descriptions of the fragment types).




25 micron

Figure 2. Red slate and carbonate containing acicular to massive hematite (H). The large dark equant bleb (Rh) is composed of rhodochrosite. The gangue (dark grey to black) also contains Fe(Mn) chlorite, Fe(Mn)K mica, quartz, and potassium feldspar (Backscatter Electron Image).

TABLE 2: Distribution and Brief Description of Fragment Types in Sample P1.

| Fragment Type | Percentage of Sample Population* | Brief Description** |
|---|---|---|
| 1 | 31.5% | Red slate with various Fe/Ti/Mn oxides. |
| 2 | 7.8% | 45-60% fine to medium-grained calcite with varying amounts of other phases such as quartz and Fe(Mn) chlorite. |
| 3 | 10.0% | 60-90% fine to medium-grained calcite with quartz, Fe-chlorite, alkali feldspar, pyrite, and traces of hematite. |
| 3(a) | 3.9% | Coarse-grained rhodochrosite with other phases such as quartz, rhodonite, and FeMn chlorite. |
| 4 | 12.3% | Red slate with massive to acicular hematite rhodochrosite, and sometimes secondary manganese oxides. |
| 5 | 3.9% | Massive Mn and Mn/Fe oxides with minor quartz, potassium feldspar, and Fe-chlorite. |
| 6 | 3.9% | Massive to spherulitic braunite with minor Mn oxides and various silicates. |
| 8 | 4.7% | Silicified slate with secondary (?) rhodochrosite. |
| 9 | 3.9% | Silicified light brown/grey slate with various Fe/Ti/Mn oxides. |

TABLE 2 (Cont'd)

| | | |
|---|---|---|
| 10 | 1.6% | Silicified chloritic slate. |
| 11 | 1.6% | Silicified slate with "swarms" of thin manganite jacobsite veins. |
| 12 | 1.6% | Green chloritic slate with minor rhodochrosite. |
| 13 | 1.6% | Metamorphosed arkose |
| 14 | 0.8% | Coarse-grained quartz with Mn chlorite (pennantite) plates and books. |
| 15 | 0.8% | Medium-grained quartz with minor fine-grained rhodochrosite and "feathery" chlorite. |
| 16 | 0.8% | Green chloritic slate with large brown "gel" pseudomorphs |
| Carbonate C | 3.1% | Cryptocrystalline to fine-grained rhodochrosite (often spherulitic) with various other phases such as quartz, rhodonite, FeMn chlorite, and minor hematite. |
| AB | 6.2% | Green slate with quartz, albite, brown "gel" pseudomorphs, and Fe/Ti oxides. |

*To calculate these percentages the surface area of all fragments was assumed to be the same. Actually they do vary somewhat (see Figure 1 for example of size variation).

**See Appendix A-2 for more details.

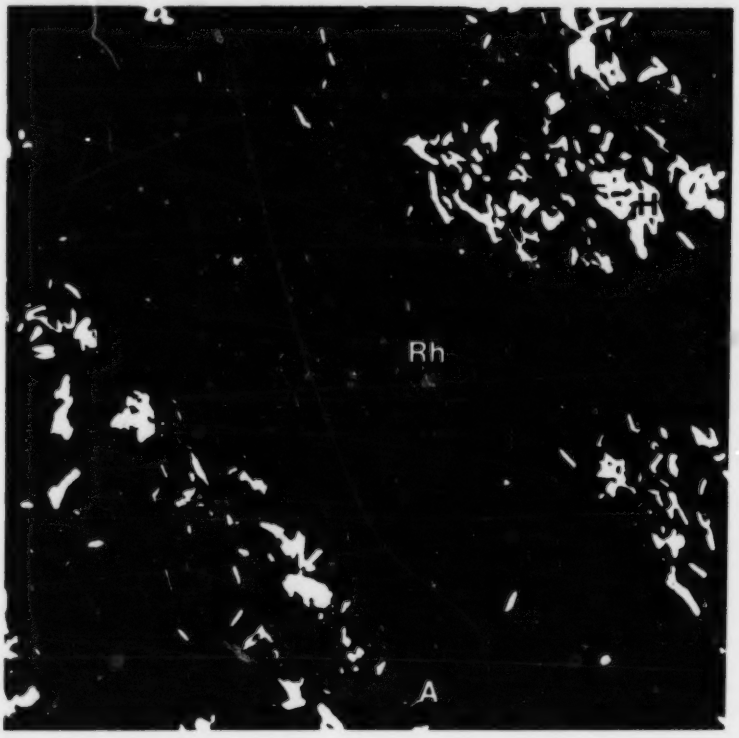
The manganese-bearing phases present in the sample are listed in Table 3 with a very general estimate of their relative abundance. The major and common minerals are listed in decreasing abundance.

The braunite is spherulitic to massive and, when it occurs, generally comprises 80-100% of the assemblage. Albite, MnKMg mica and minor MnCaAl silicate are present as interstitial material. Minor inclusions of fine acicular to tabular pyrolusite were observed in half the braunite fragments. One fragment contained only 45-55% spherulitic braunite and a small amount (-1-5%) of equant manganite blebs (from 10 to 50 micron across) found in the gangue material.

Rhodochrosite (with minor Ca) is present in various forms (see Table 2 for list of fragment types). The most common occurrence of this mineral is in fragments where it comprises 50-100% of the material. In these fragments it is coarse-grained or cryptocrystalline (often spherulitic) and is associated with quartz, rhodonite, FeMn chlorite, alkali feldspar, and white mica or manganophyllite. With the coarse carbonate these minerals occur as fine to medium-grained masses and with the cryptocrystalline masses they are fine (1-15 micron range) interstitial material. The latter fragment type also may contain minor concentrated hematite, manganite veins (30-60 micron wide), or Fe oxide. The rhodochrosite also occurs as the predominant gangue mineral in the hematite-rich red slates (see Figure 3). It is finely intergrown (10-25 micron range) with Fe(Mn) chlorite, quartz, potassium feldspar, and Fe(Mn) K mica, but may occur as large (25-60 micron), spongy, equant blebs (spherulitic). Traces of apatite have been observed. Secondary manganite may be present as small, equant blebs 10-50 micron across or, as in one case, large lenses of intruding material with acicular hematite inclusions. A large hausmannite and pyrolusite vein 25-50 micron wide was found in one fragment. Traces of euhedral to subhedral magnetite have been observed also.

TABLE 3 Manganese-Bearing Phases in Plymouth 1 Sample

| Mineral | Ideal Formula | Relative Abundance | In Fragment Type(s): |
|---|---|---|---|
| Rhodochrosite (Ca) | $MnCO_3$ | major | 1,3(a),4,8,12,15,Carbonate C |
| Braunite | $(Mn, Si)_2O_3$ | major | 6 |
| Fe(Mn)Chlorite | $(Mg,Al,Fe,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | major | 2,3(a),4,8,13,Carbonate C |
| Psilomelane (Ca) | hard manganese oxides | common | 1,4,5 |
| Pyrolusite | $MnO_2$ | common | 1,4,5,6,9 |
| Manganite | MnO(OH) | common | 1,4,5,11,Carbonate C |
| Hausmannite | $Mn_3O_4$ | trace | 4 |
| Bixbyite | $(Mn,Fe)_2O_3$ | trace | 5 |
| Jacobsite | $MnFe_2O_4$ | trace | 9,11 |
| Mangansilmenite | $(Fe,Mn)TiO_3$ | trace | 1,9 |
| Rhodonite | $MnSiO_3$ | trace | 1,3a,Carbonate C |
| Bustamite | $(Mn,Ca,Fe)SiO_3$ | trace | 1 |
| MnCaAl Silicate | ? | trace | 6 |
| MnFe chlorite | $(Mg,Al,Fe,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | trace | 1 |
| Mn chlorite (pennantite) | $(Mg,Al,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | trace | 14 |
| Manganophyllite | $K_2(Mg,Fe,Mn)_6[Si_6Al_2O_{20}](OH,F_4)$ | trace | 6 |
| MnFe (Mg) chlorite | $(Mg,Al,Fe,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | trace | Carbonate C |
| FeK(Mn)Mg mica | ? | trace | AB |




12.5 micron

Figure 3. Hematite-rich red slate with rhodochrosite. A detailed view of one fragment shows the pervasive nature of the rhodochrosite (Rh). The slightly lighter portions (A) of the rhodochrosite contain minor iron along with minor calcium. The bright acicular (H) grains are hematite. The black portions of the photograph is composed of quartz, potassium feldspar, and minor chlorite (Backscatter Electron Image).

Approximately 30-75% of some silicified green slates, containing intergrown quartz, minor albite, Fe chlorite, and KFe mica, is secondary rhodochrosite. Other chloritic slates contain minor intergrowths of the phase. Fine-grained rhodochrosite is sometimes associated with medium-grained quartz and chlorite. Finally, trace amounts of intergrown rhodochrosite and rhodonite occur as small subequant blebs (30 to 200 micron across) in the red slate containing Mn/Fe/Ti oxides.

The Fe(Mn) chlorite in this sample generally occurs finely intergrown with quartz, alkali feldspar, micas (such as phlogopite, manganophyllite, and muscovite), and calcite in green chloritic slates, calcite-rich fragments, cryptocrystalline rhodochrosite-rich fragments, the matrix of metamorphosed arkose, and hematite-rich red slate. It also infrequently occurs as large (25-150 micron across) "fans" in medium-grained calcite-rich and coarse-grained rhodochrosite-rich fragments.

The common manganese oxide minerals, psilomelane, pyrolusite, and manganite appear to occur as secondary phases in various fragment types. The psilomelane occurs as subequant to equant blebs (25-60 micron across) in 20% of the red slate with Mn/Fe/Ti oxide fragments and 5% of the hematite-rich red slate fragments. It also occurs in one fragment of the latter type as very large irregular blebs with acicular hematite inclusions. Most of the psilomelane occurs with minor pyrolusite and bixbyite intergrowths as massive, blocky material. One fragment contains matted clumps of bixbyite or hematite. Another contains a minor amount of subequant manganite blebs 50-100 micron across and only approximately 60% intergrown psilomelane and pyrolusite with finely intergrown quartz, alkali feldspar, and Fe chlorite.

The pyrolusite generally occurs as intergrowths with other manganese oxides. It is found in thin (1-5 micron across) manganite veins in 10% of the red slate with Fe/Ti/Mn oxide fragments and in a larger (25-50 micron across) hausmannite vein

in one fragment of hematite-rich red slate. Approximately 10% of the massive, blocky manganese oxides mentioned in the previous paragraph is pyrolusite. Somewhat tabular pyrolusite grains are present in minor amounts (<1%) as inclusions in half of the massive braunite fragments and as scattered grains in most of the light brown/grey silicified slate fragments.

The manganite most often occurs as small (10-100 micron) subequant blebs. The blebs are found in small amounts (<1%) in approximately 20% of the red slate with Mn/Fe/Ti oxides and the hematite-rich red slate. One fragment of the latter type contains a massive manganite intrusion intergrown with remobilized hematite. A small number of the blebs are also, as mentioned previously, associated with the massive, blocky manganese oxides and the massive braunite. The manganite also occurs as thin (1-5 micron across) veins in small amounts (<1%) of 10% of the fragments of red slate with Mn/Fe/Ti oxides and in larger amounts (15-20%) as swarms with jacobsite intergrowths in a few silicified slate fragments (see Figure 4). Finally, very minor manganite in vein/lense form (30-60 micron across) has been observed in the cryptocrystalline (often spherulitic) rhodochrosite fragments.

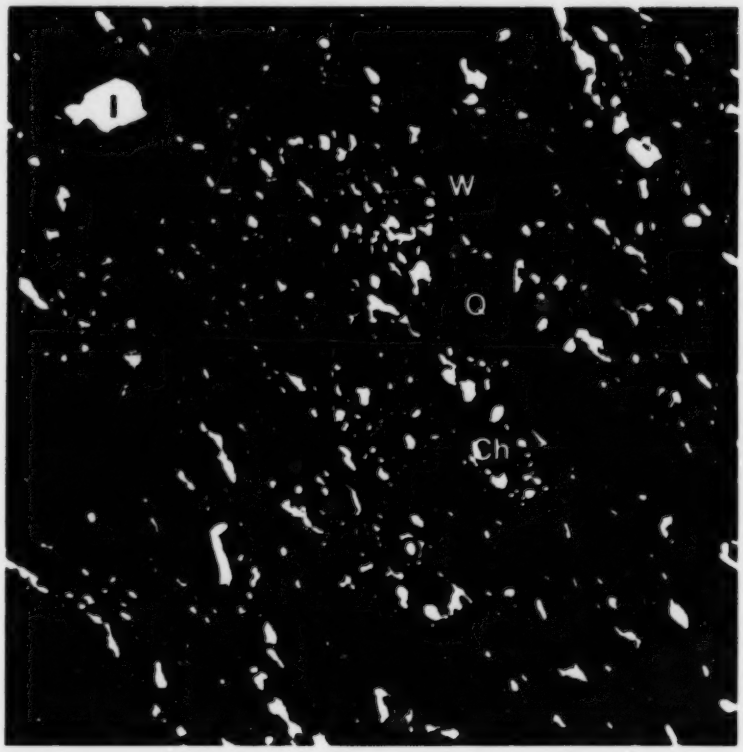
The remaining manganese-bearing phases occur in trace amounts only and are found in a variety of fragment types as listed in Table 3. For details on their association, if not already mentioned, see Appendix A-2.

4.1.2 Plymouth 2

The Plymouth 2 sample population contains 17 fragment types. The most abundant are as follows:

(a) Red slate with varying amounts of Fe/Ti oxides, secondary manganese oxides, and in some cases Mn chlorite (pennantite) and Mn(K)Al Silicate (see Figure 5).

Figure 4. Thin manganite (M) and minor jacobsite (J) veins in silicified slate. The large subequant grains (Q) are quartz. (Backscatter Electron Image).




12.5 micron

Figure 5. Red slate containing Fe/Ti oxides. The dark lenticular grains (Q) are quartz or albite and the interstitial lighter material is K(Fe,Mg) mica (W) with minor slightly brighter Fe-chlorite (Ch). The large, somewhat square grain in the upper left-hand corner and the more elongate to acicular grains are FeTi ilmenite (I). The more equant and rounded grains are Fe oxide (O). (Backscatter Electron Image).

(b) Spherulitic to massive braunite with intergrown FeMn chlorite, K(Fe,Mn)Mg mica, quartz, albite and MnAl Silicate along with minor barite, MnBa sulphate(As,Rb), hematite, and manganite.

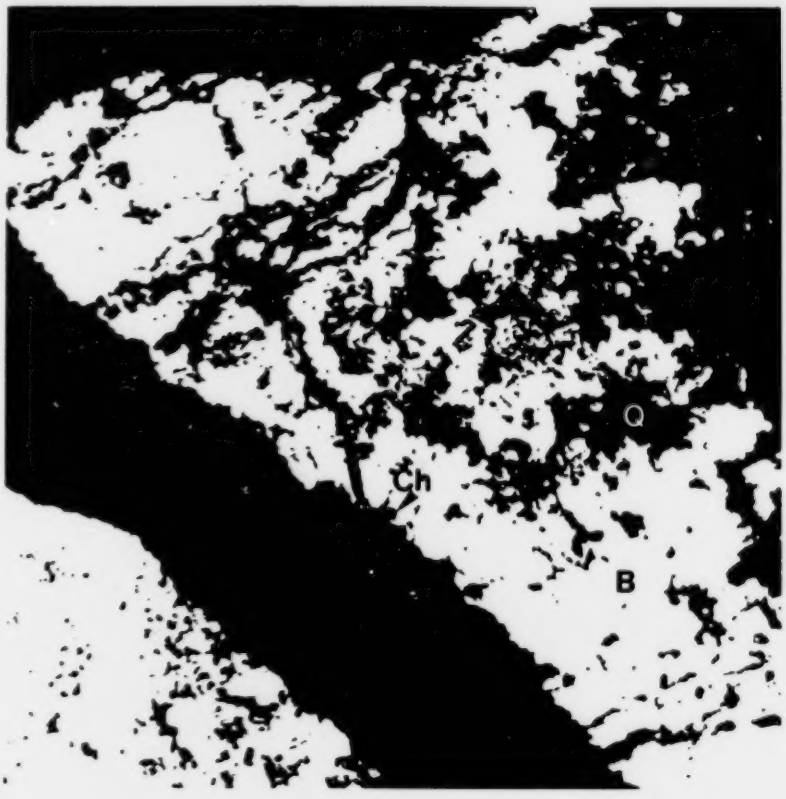
(c) Fine to coarse-grained calcite with anywhere from 0 to 20% interstitial phases such as quartz, Fe-chlorite, albite, and K(Fe) mica in various combinations.

(d) Green chloritic slates with a variety of inclusions such as irregular calcite blebs, brown "gel" pseudomorphs, and FeMn oxides and braunite.

These fragment types make up approximately 80% of the sample. The remaining fragments are comprised of a variety of slates, fine to coarse-grained quartz with or without albite and manganite, mat chlorite with quartz and K(Fe) mica, cryptocrystalline rhodochrosite and subhedral to anhedral braunite in layers with quartz, albite, Mn chlorite and barite (see Table 4 for distribution and brief descriptions of the fragment types).

The manganese-bearing phases present are listed in Table 5 with a general estimate of their distribution. The major and common minerals are listed in decreasing abundance.

Braunite, often with very minor calcium, is the most abundant of all the manganese-bearing phases present. It most frequently occurs as a spherulitic to massive aggregate (see Figure 6) comprising 40-95% of the fragment (generally >70%). Quartz, albite, Fe chlorite, Mn chlorite, MnAl Silicate, and K(Fe,Mn)MgAl mica in various combinations are finely intergrown and interstitial to the braunite. 25% of the fragments contain traces of acicular hematite as inclusions in the braunite. Another 25% contain minor amounts of small blebs (5-30 micron across) or thin veins (1-5 micron across) of manganite. Traces of barite and MnBa(As,Rb) sulfate have also been observed.




125 micron

Figure 6. Spherulitic to massive braunite (B) with interstitial quartz (Q), minor albite (not discernible from quartz in this picture), and Fe-chlorite (Ch). (Backscatter Electron Image).

TABLE 4: Distribution and Brief Description of Fragment Types in Sample P2.

| Fragment Type | Percentage of Sample Population*** | Brief Description** |
|---|---|---|
| 1 | 17.8% | Red slate with various Fe/Ti/Mn oxides, secondary Mn oxides, and often Mn(K)Al Silicate. |
| 1(a) | 24.3% | Red slate with more Fe/Ti oxides and secondary Mn oxides. |
| 2 | 10.3% | Fine to coarse-grained calcite with 0-20% interstitial quartz and chlorite. |
| 3 | 3.2% | Fine to medium-grained calcite with >20% albite, Fe chlorite, K(Fe) mica and quartz in various combinations. |
| 4 | 13.0% | Spherulitic to massive braunite with intergrown gangue of various micas, quartz and albite; and minor Fe and Mn oxides. |
| 4(a) | 1.1% | Subhedral to anhedral braunite in finely intergrown quartz, albite, Mn chlorite, and barite. |
| 5 | 6.2% | Light brown silicified slate with 10-15% Fe/Ti oxides. |
| 6 | 2.2% | Silicified red/brown slate with minor Fe/Ti/Mn oxides and secondary manganite. |

TABLE 4 (Cont'd)

| | | |
|---|---|---|
| 7 | 5.4% | Medium to coarse-grained quartz. |
| 8 | 3.2% | Green chloritic slate with brown "gel" pseudomorphs, and minor Fe/Ti oxides and pyrite. |
| 10 | 1.1% | Mat Fe chlorite with quartz, K(Fe) mica, and minor Ti/Fe oxides. |
| 11 | 1.4% | Fine to medium-grained albite and quartz with approximately 20% secondary manganese oxides. |
| 12 | 5.4% | Green silicified chloritic slate with irregular calcite blebs. |
| 13 | 1.1% | Cryptocrystalline rhodochrosite with local interstitial quartz. |
| 14 | 1.1% | Green chloritic slate with brown "gel" blebs of intergrown calcite and Fe oxide. |
| 15 | 3.2% | Chloritic slate with hematite, braunite, psilomelane, and pyrolusite. |

***See * in Table 1.

**See Appendix A-2 for more details.

TABLE 5 Manganese-Bearing Phases in Plymouth 2 Sample

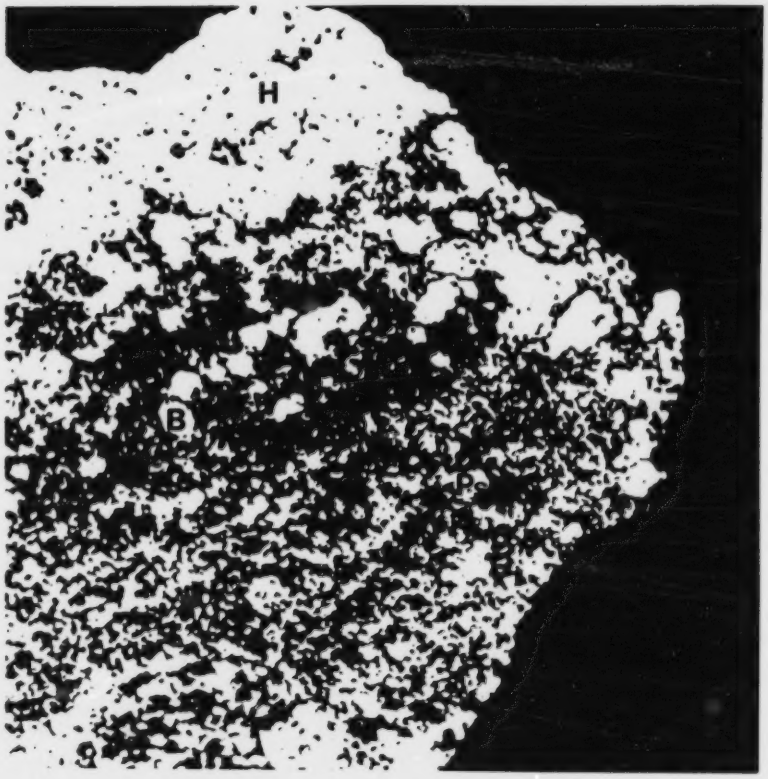
| Mineral | Ideal Formula | Relative Abundance | In Fragment Type(s): |
|---|---|---|---|
| Braunite | $(Mn,Si)_2O_3$ | major | 4,4a,15 |
| Mn chlorite | $(Mg,Al,Fe,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | major | 1,4,4a,15 |
| Manganite | MnO(OH) | common | 1,1a,4,11 |
| Psilomelane | hard manganese oxides | common | 1,1a,15 |
| Mn(K)Al silicate | ? | common | 1,4 |
| Rhodochrosite | $MnCO_3$ | common | 13 |
| Pyrolusite | | common | 1,1a,11,15 |
| Fe(Ti,Mn) oxide (hematite) | $Fe_2O_3$ | trace | 1 |
| CrMnFeZn oxide (chronite) | $FeCr_2O_4$ | trace | 1a |
| MnBa sulphate (As,Rb) | ? | trace | 4 |
| MnFe(Ca) chronite | $(Mg,Al,Fe,Mn,Ca)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | trace | 6 |

This major manganese mineral also occurs as subhedral to anhedral grains or small equant blebs 15 to 40 micron across (opherulitic) associated with acicular to anhedral layered hematite and finely intergrown psilomelane and pyrolusite in veins 20-40 micron across or large irregular blebs (100-300 micron long) (see Figure 7). Both textures occur in finely intergrown (5-40 micron range) quartz, albite, and Mn chlorite. The former fragment type also contains minor barite.

Mn chlorite (pennantite), although a major manganese-bearing phase, is much less abundant than braunite. It occurs, as mentioned above, as one of the intergrown gangue minerals in all braunite-bearing fragments. It is also present in the red slate with small amounts of Fe/Ti oxides as fine (5-15 micron range) intergrowths with quartz and K(Fe,Mg) mica.

All the common manganese-bearing minerals appear to be secondary phases in various fragment types. The most abundant, manganite, occurs as thin veins 1-5 micron across, often with minor psilomelane, in 30-50% of the fragments of red slate with Fe/Ti oxides. Two of these fragments contain thick veins 10-25 micron across with finely intergrown pyrolusite or psilomelane. One third of them contain approximately 1% manganite in the form of small equant blebs (10 to 25 micron across) with local psilomelane or pyrolusite inclusions. As mentioned previously, thin veins or small equant blebs are also present in 25% of the spherulitic to massive braunite fragments. Finally, one fragment of fine to medium-grained albite and quartz contains a spongy vein/lense (25-75 micron across) of intergrown manganite and minor pyrolusite.

The psilomelane, as well as occurring as the minor inclusions mentioned above, may be present as the most abundant manganese oxide in the two fragment types. One fragment of red slate with more Fe/Ti oxides contains approximately 5% psilomelane in the form of subequant blebs (10-25 micron across) and psilomelane




125 micron

Figure 7. Irregular hematite (H) with small braunite (B) blebs, intergrown psilomelane (Ps) and very minor pyrolusite with dark interstitial quartz, Mn (Fe) chlorite, and albite. The gangue minerals are not distinct from each other in this photograph. (Backscatter Electron Image).

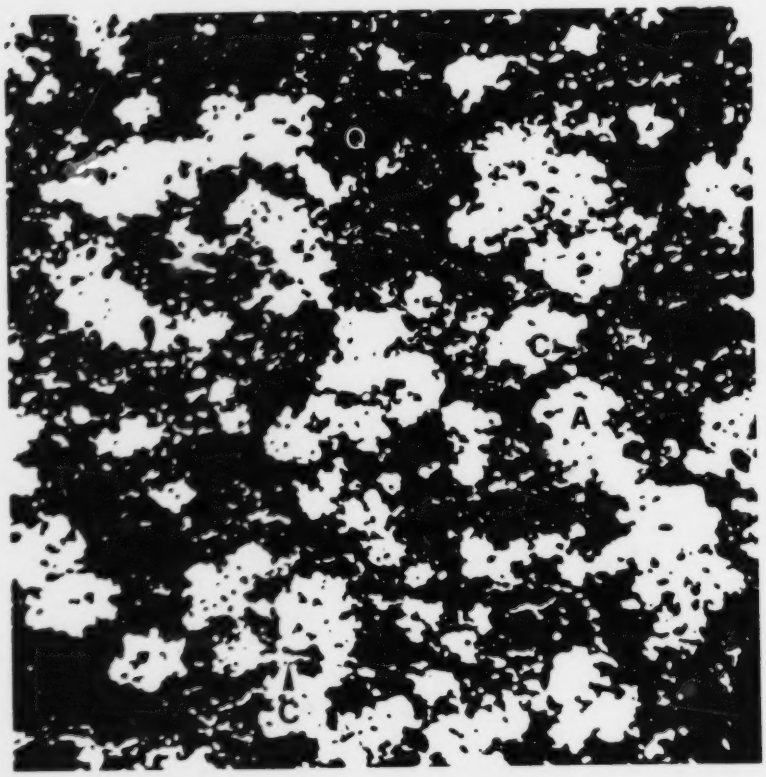
finely intergrown with very minor pyrolusite occurs as veins 20-40 micron across and large subequant blebs 100-300 micron across in the chloritic fragments containing hematite and braunite (see Figure 7).

Pyrolusite occurs as inclusions in and intergrowths with manganite and psilomelane. All occurrences have been mentioned above.

The Mn(K)Al silicate is found in the red slate with minor Fe/Ti oxides and the gangue of the spherulitic to massive braunite. In the red slate it appears to be a secondary mineral overprinting the intergrown quartz, Mn chlorite, K(Fe,Mg) mica and albite (see Figure 8). It occurs in 25% of the fragments and comprises 10-30% of these grains. However, the Mn(K)Al silicate is only a minor component, at most 5%, in the gangue material of the braunite fragments. It is finely intergrown (5-15 micron range) with quartz, albite, Fe chlorite or Mn chlorite, and K(Fe,Mn)Mg mica.

The final common manganese-bearing phase, rhodochrosite (with minor calcium), is present in very minor (although not trace) amounts. This cryptocrystalline carbonate comprises approximately 85% of the fragments it is contained in, the remaining material being coarsely intergrown quartz.

The remaining minerals listed in Table 5 are present in trace amounts in various fragment types as indicated. For details on their association, if not previously mentioned, see Appendix A-2.




50 micron

Figure 8. Spongy blebs of Mn(K)Al silicate (A) overgrown on finely intergrown K(Mn,Fe,Mg) mica (C), quartz (Q), and albite (not discernible from quartz in this picture). (Backscatter Electron Image).

4.1.3 Plymouth 3

The Plymouth 3 crushed ore sample population contains 18 fragment types. The most abundant are:

(a) Dark red manganiferous slate with varying amounts of MnAl silicate, rhodochrosite, ilmenite, mangonoilmenite and secondary Mn-oxides such as manganite and psilomelane.

(b) Red slate with very minor rhodochrosite, hematite, ilmenite, Ti oxide, and secondary Mn oxides (see Figure 9).

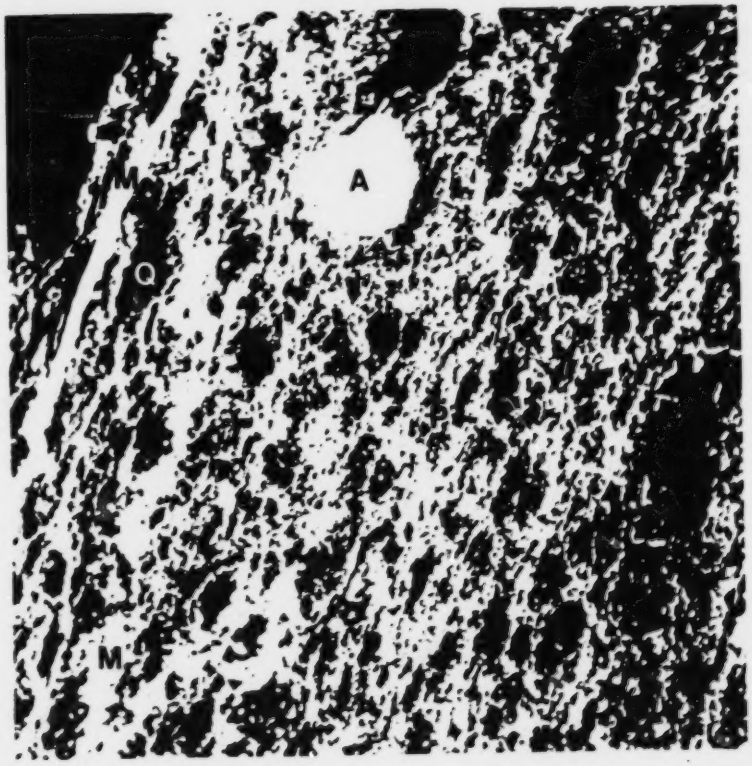
(c) Red slate with 20-80% layered irregular, acicular or massive hematite, rare euhedral to subhedral magnetite, secondary Mn-oxides, and minor braunite.

(d) Silicified green chloritic slate with various secondary Mn-oxides, Ti oxide, ilmenite, pyrite, minor albite, trace apatite, and minor calcite.

These fragments comprise approximately 75% of the sample population. The remaining fragments are made up of various chloritic slates, medium to coarse-grained quartz, predominantly secondary Mn oxides with quartz, 30-98% fine to cryptocrystalline, mat chlorite, medium-grained calcite, and irregular or medium-grained hematite-rich grains (see Table 6 for distribution and brief descriptions of the fragment types).

The manganese-bearing phases in this sample are listed in Table 7 with a general estimate of their relative abundances. The major and common minerals are listed in order of decreasing abundance.

The major phases, manganite, rhodochrosite and psilomelane, are all present in similar amounts. Manganite, which appears to be the most abundant, is present in a large variety of grain types and forms. It most commonly occurs as small subequant to equant




50 micron

Figure 9. Red slate with Fe/Ti oxides. Finely intergrown FeK mica (P), quartz (Q), and albite (not discernible from quartz). The large white equant grain (A) is apatite. The white vein and irregular blebby "vein" are composed of manganite (M). The remaining small bright grains are hematite, ilmenite, Ti oxide and minor apatite. (Rackscatter Electron Image).

TABLE 6: Distribution and Brief Description of Fragment Types in Sample P3.

| Fragment Type | Percentage of Sample Population*** | Brief Description** |
|---|---|---|
| 1 | 20.9% | Red slate with minor rhodochrosite, Fe/Ti oxides, and secondary Mn oxides. |
| 2 | 31.9% | Darker, more manganiferous red slate with rhodochrosite, Mn/Fe/Ti oxides, and secondary Mn oxides. |
| 3 | 1.4% | Green chloritic slate with medium-grained quartz and plagioclase grains, and brown Fe oxide "gel". |
| 4 | 11.4% | Red slate with layered hematite, rare magnetite, braunite and secondary Mn oxides. |
| 5 | 5.0% | Medium to coarse-grained quartz with various other phases such as albite, calcite, apatite, chlorite, Fe oxide and secondary Mn oxide. |
| 6 | 4.0% | Various Mn oxides in quartz and albite or quartz and MnCaAl silicate. |
| 7 | 0.7% | Green chloritic slate with minor calcite, quartz, albite, and Fe oxide. |
| 10 | 10.7% | Silicified green chloritic slate with various secondary Mn oxides, Fe/Ti oxides, pyrite, minor albite, trace apatite, and minor calcite. |

TABLE 6 (Cont'd)

| | | |
|---|---|---|
| 12 | 2.8% | 90-98% fine-grained rhodochrosite with quartz, albite, Fe chlorite, Fe oxide, and pyrite. |
| 13 | 1.4% | Finely intergrown quartz and chlorite with overgrown brown "gel". |
| 14 | 1.7% | Finely intergrown albite, apatite, apatite (Mn) and minor rhodochrosite (15 to 40% of each fragment) with irregular hematite and minor psilomelane grains. |
| 15 | 0.7% | Large subhedral magnetite and acicular hematite in finely intergrown quartz, albite and KFeMg mica. |
| 16 | 0.7% | Brown slate(?) with 25-35% spongy rhodochrosite overgrown on quartz, albite, Fe(Mn)KMg mica and magnetite (Mn, Ti). |
| 17 | 3.2% | Light brown/green slate with minor Fe/Mn/Ti oxides and braunite. |
| 18 | 1.4% | Mat Fe chlorite with minor interstitial quartz, KFe mica, and CaFeAl silicate. |
| 19 | 0.7% | Green chloritic slate with secondary Mn oxides. |
| 20 | 0.7% | Fine green chloritic slate with AlFe(Mg)Si phosphate, secondary manganite, and Fe/Ti oxides. |
| 22 | 0.7% | Medium-grained calcite. |

***See * in Table 1.

**See Appendix 1 for more details.

blebs approximately 10 to 100 micron across and never more than about 2% of the fragment. These are found in 20% of the dark red slates with, in two cases, intergrown pyrolusite; many of the fragments of quartz with secondary Mn oxides; 20% of the layered hematite-rich red slate with minor intergrown jacobsite in the blebs; 7% of the silicified green chloritic slates with minor Fe/Ti oxides and pyrite; and rarely in the light brown/green slate with Fe/Mn/Ti oxides. Small manganite veins from 1 to 5 micron across are also commonly seen and are never more than approximately 2% of the fragment. They occur in 25% of the red slate with Fe/Ti oxides (see Figure 9) along with, in one case, minor psilomelane intergrowths; 33% of the dark red slate; 20% of the silicified green chloritic slates with minor Fe/Ti oxides and pyrite (see Figure 10); and in the one fragment of fine green chloritic slate intergrown with pyrolusite. Rarely, masses or intruding lenses of finely micron intergrown 5-50 micron range manganite, psilomelane and minor pyrolusite occur in medium to coarse-grained quartz often with various phases such as MnCaAl Silicate, calcite, apatite and chlorite; or in silicified green chloritic slate with Fe/Ti oxides and small amounts of other phases such as pyrite, albite, apatite, and calcite. Finally, manganite is present as a small lense 59-100 micron wide at one end of a fragment of fine green chloritic slate.

Rhodochrosite, which appears to be slightly more abundant than the psilomelane, also occurs in a variety of fragment types and forms. Most commonly it is fine-grained with minor interstitial quartz, albite, and chlorite. Often large (25-60 micron across) euhedral to subhedral Fe oxide and pyrite crystals are present in minor amounts. Large (25-100 micron across) spongy subequant blebs of rhodochrosite are found in the red slate with Fe/Ti oxides in trace amounts; the dark red slate is in approximately 1-2% of the fragments; and in the brown slate as an overgrowth of approximately 25-35% of the fragment. The hematite-rich red slate sometimes contains small amounts (approximately 5-10%) of rhodochrosite intergrown with quartz,

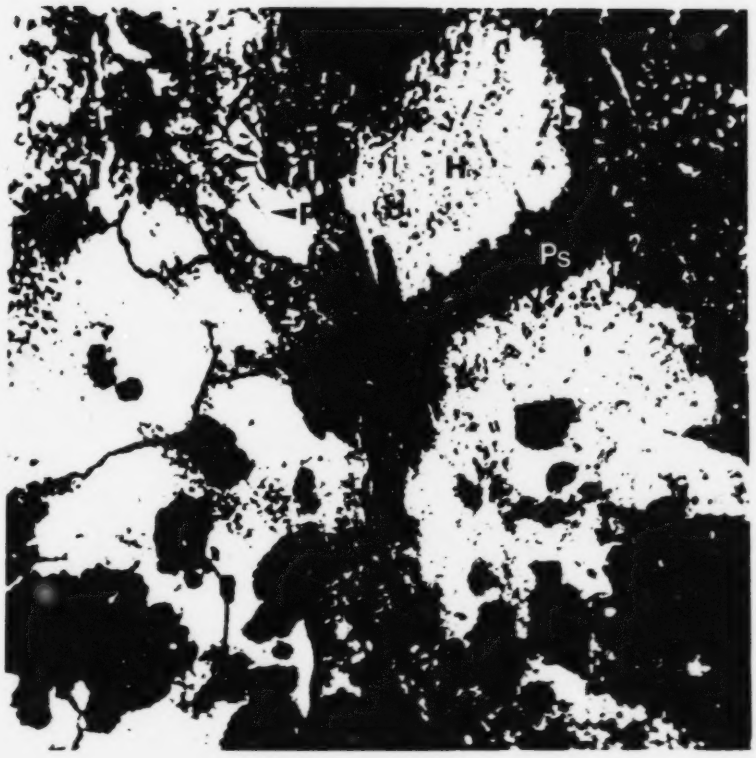
TABLE 7: Manganese-Bearing Phases in Plymouth 3 Sample

| Mineral | Ideal Formula | Relative Abundance | In Fragment Type(s): |
|---|---|---|---|
| Manganite | $MnO(OH)$ | major | 1,2,4,5,6,10,17,19,20 |
| Rhodochrosite | $MnCO_3$ | major | 1,2,4,12,16 |
| Psilomelane | hard manganese oxides | major | 1,2,5,6,10,14 |
| Fe(Mn) Chlorite | $(Mg,Al,Fe)_{12}[(Si,Al)_8 O_{20}](OH)_{16}$ | common | 2,10 |
| Hausmannite | $Mn_3O_4$ | common | 6 |
| Pyrolusite | $MnO_2$ | common | 2,6,10,19 |
| Bixbyite | $(Mn,Fe)_2O_3$ | trace | 2,6 |
| Jacobsite | $MnFe_2O_4$ | trace | 4,6,15 |
| Manganoilmenite | $(Fe,Mn)TiO_3$ | trace | 2,10 |
| Magnetite (Mn,Ti) | $Fe_3O_4$ | trace | 16 |
| Braunite | $(Mn,Si)_2O_3$ | trace | 9,17 |
| MnAl Silicate | ? | trace | 2,4 |
| MnCaAl Silicate | ? | trace | 6,17 |
| Fe(Mn)KMg mica | ? | trace | 16 |
| MnFeKMg mica | ? | trace | 17 |
| MnCa Phosphate (apatite) | $Ca_5(PO_4)_3(OH,F,Cl)$ | trace | 14 |

MnAl silicate, KFeMg mica, and albite, with minor apatite and Fe chlorite.

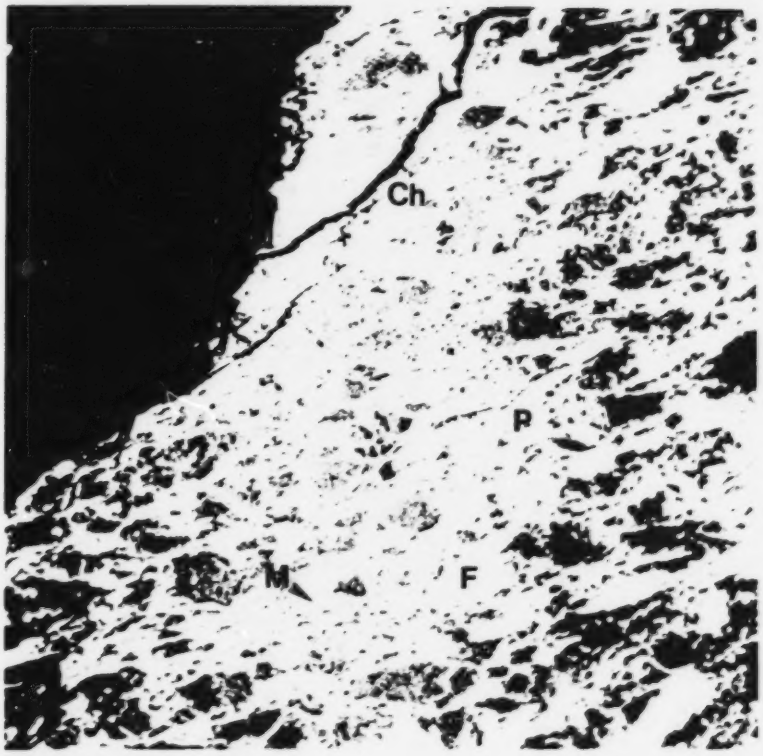
Psilomelane, the least abundant of the major manganese-bearing phases, also occurs in a variety of forms and fragment types. The occurrences of fine veins of mixed manganite/psilomelane and intergrown psilomelane, manganite, and minor pyrolusite masses or intruding lenses are described above. This phase is also present as minor subequant to equant blebs from 10 to 100 microns across in 10% of the dark red slate fragments and 15% of the quartz, albite, or MnCaAl silicate, and manganese-oxide fragments. In the latter the blebs contain pyrolusite inclusions. This fragment type also contains one grain composed of massive hausmannite with psilomelane rims and minor pyrolusite inclusions (see Figure 10), and several grains containing thin (1-10 micron wide) veins locally associated with similar jacobsite veins. The veins never comprise more than approximately 2-3% of the fragment. Similarly, the irregular hematite-rich fragments contain approximately 2-3% psilomelane in the form of small (1-10 micron across) irregular blebs overgrown on the finely intergrown albite, apatite, apatite (Mn) and minor rhodochrosite.

Chlorite, rich in iron with minor manganese, is the most abundant of the common manganese-bearing phases. It is finely intergrown (1-10 micron range) with albite, quartz, FeK(Mg) mica local rhodochrosite, and trace MnAl silicate in the dark red slate fragments. Approximately 20% of these fragments also contain up to 2% large chlorite "fans" 25-75 micron long (see Figure 11). The silicified green chloritic slate contains this Fe(Mn) chlorite finely intergrown (5-20 micron range) with K(Fe) mica, quartz, albite, apatite and locally calcite (see Figure 11). Again large "fans" of chlorite and, in this case, chlorite and K(Fe) mica are often present.




50 micron

Figure 10. Massive hausmannite (H) with psilomelane (Ps) rims and minor pyrolusite (P). The dark gangue minerals are albite and MnCaAl silicate. The bright irregular grains in the upper left-hand corner are hematite. (Backscatter Electron Image).




50 micron

Figure 11. Silicified green chloritic slate of finely intergrown K(Fe) mica (P), slightly lighter Fe(Mn) chlorite (Ch), quartz (Q), and alkali feldspar (not discernible from quartz). The fine bright veins (M) are of manganite. The remaining bright grains are Fe oxide, Ti oxide, ilmenite and manganoilmenite. Notice the large chlorite and chlorite/K(Fe) mica "fans"(F). (Backscatter Electron Image).

Hausmannite (see Figure 10) and pyrolusite are the other common manganese-bearing phases in this sample. They are always associated with other manganese oxides and all these occurrences have been described in the above paragraphs.

The remaining minerals are present in very small amounts in various forms and fragment types, many of which have been mentioned above. In general they occur either finely intergrown with the other minerals of the fragments or as irregular to acicular grains 5-25 micron long scattered through the fragments. See Table 7 and Appendix A-2 for more details.

4.1.4 Plymouth 4

The sample population from the Plymouth 4 crushed ore contains 18 fragment types. The most abundant of these are:

(a) Fragments containing 15-90% Mn/Fe oxides with a variety of gangue minerals such as quartz, KFe(Mn) mica, alkali feldspar, rhodochrosite, Fe chlorite, and minor apatite.

(b) Cryptocrystalline or medium-grained manganese-rich siderite with various amounts of quartz, chlorite Fe(Mg) mica, Fe(Mn) Al silicate, jacobsite, pyrite, and chalcopyrite.

(c) Silicified red slate with or without rhodochrosite along with various amounts of Fe oxide, Ti oxide, ilmenite, and manganite.

These fragments make up approximately 60% of the sample population. The remaining fragments are comprised of various light chloritic slates, dark grey manganiferous slate, fine to medium-grained iron-rich rhodochrosite or rhodochrosite (with minor Ca) intergrown with minor amounts of other phases, mat Fe Mn chlorite, and fine to coarse-grained quartz with various other minerals (see Table 8 for distribution and brief description of the fragment types).

The manganese-bearing phases present in this sample are listed in Table 9 with a very general estimate of their relative abundances and with the fragment types they are found in. The major and common minerals are listed in order of decreasing abundance.

Manganese-rich siderite, the most abundant of all the phases listed, is present in two forms. The most common of these is as cryptocrystalline crystals intergrown with Fe chlorite, Fe(Mg) mica, and quartz (see Figure 12). The siderite is 45-95% of each fragment. Large quartz grains, chlorite "fans" 50-100µm long, and a thin 10-25µm wide calcite vein have been observed along with traces of chalcopyrite, framboidal or subhedral pyrite, and irregular or acicular jacobsite grains. Medium-grained manganese-rich siderite intergrown with Fe-rich chlorite, quartz, and potassium feldspar is also present in the ore. Minor dark Fe(Mn)Al silicate grains have been observed in the siderite grains.

Rodochrosite with minor calcium is also very abundant in this sample. Most commonly it occurs in fragments as the major mineral intergrown with quartz and FeMn chlorite. These minerals are all fine to medium-grained. Anhedral Fe oxide with pyrite cores, euhedral to subhedral magnetite, and subhedral pyrite are found in layers of these fragments.

The rhodochrosite also occurs finely intergrown with other phases in various fragment types. It is a common mineral in the hematite-rich dark grey/red slate intergrown with MnCa silicate, minor FeCa phosphate, quartz and FeK(Mg) mica (see Figure 13). It is locally intergrown with quartz and alkali feldspar or Fe-chlorite in the manganese oxide-rich fragments. Large equant spongy grains 30-75 micron across of rhodochosite with minor MnCa silicate are present in much of the silicified red slate (see Table 8). And finally, one fragment of the fine to

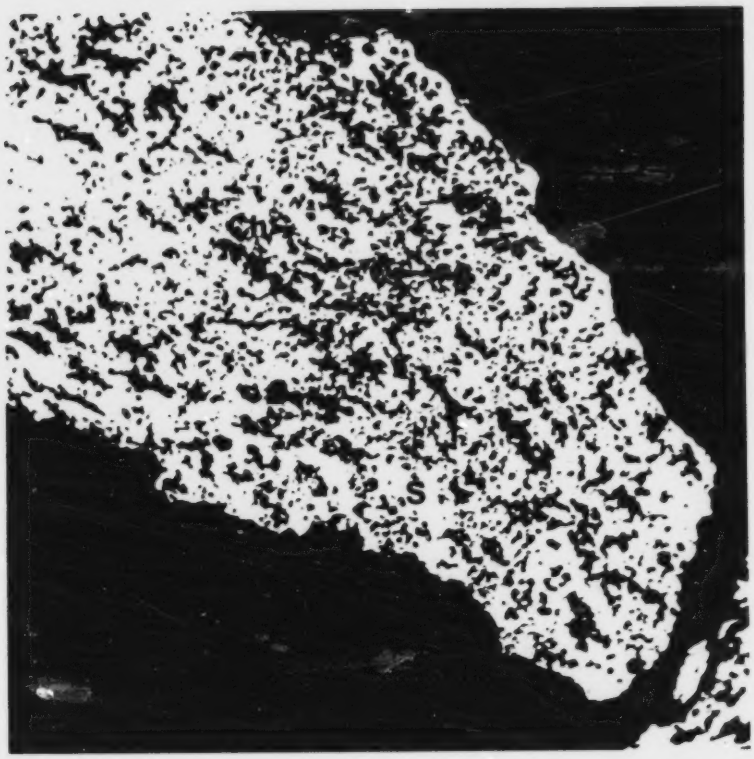



Figure 12. Cryptocrystalline manganese-rich siderite (S) intergrown with Fe chlorite (Ch), Fe(Mg,Al) silicate (not discernable from chlorite), and quartz (Q). (Backscatter Electron Image).

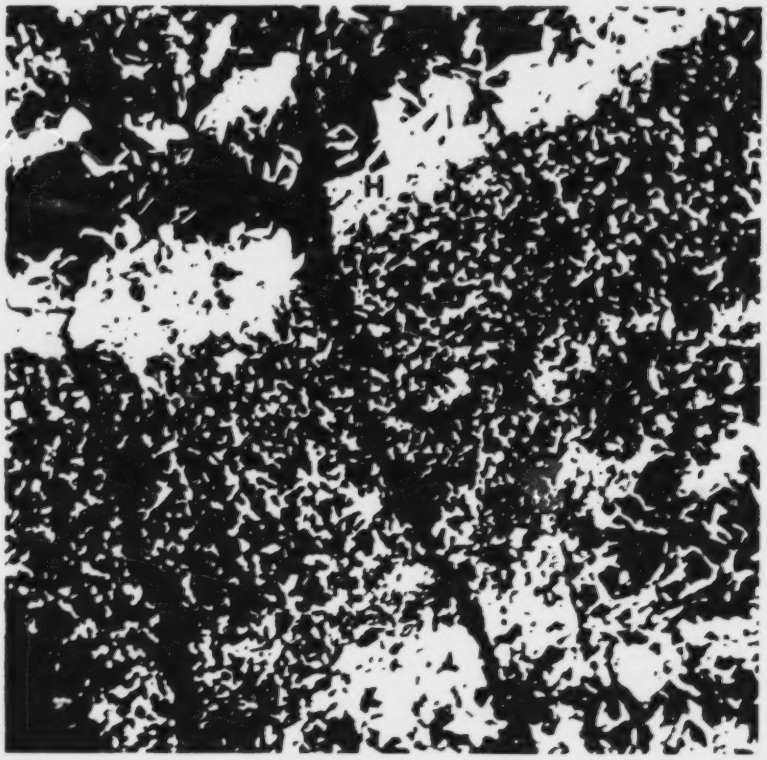



Figure 13. Hematite(H)-rich dark grey/red slate with finely intergrown rhodochrosite (with minor calcium) and MnCa silicate (Rh) (not distinct in this photograph). Minor FeCa phosphate (P) is also present. (Backscatter Electron Image).

TABLE 8: Distribution and Brief Description of Fragment Types in Sample P4.

| Fragment Type | Percentage of Sample Population*** | Brief Description** |
|---|---|---|
| 1 | 12.7% | Silicified red slate with rhodochrosite, minor Fe/Ti oxides and manganite. |
| 1a | 4.9% | Silicified light red slate without rhodochrosite, and with less Fe/Ti oxides and manganite than in Type 1. |
| 1b | 1.0% | Silicified dark red slate without rhodochrosite, and with more Fe/Ti oxides and manganite than in Type 1. |
| 2 | 6.9% | Medium-grained Mn-rich siderite, Fe-rich chlorite, potassium feldspar, quartz and minor Fe(Mn) Al silicate. |
| 3 | 1.0% | Medium-grained quartz with K(MgFe) mica and various Fe/Mn oxides. |
| 4 | 3.4% | Brown/green slate with numerous brown "gel" blebs and minor manganite. |
| 5 | 21.4% | From 15-90% Mn/Fe oxides with a variety of gangue minerals such as quartz, rhodochrosite, and mat chlorite. |
| 6 | 13.7% | Very dark grey/red slate with irregular elongate to massive hematite along with various Mn oxides and often rhodochrosite. |
| 7 | 1.0% | Very fine-grained green chlorite slate. |

TABLE 8 (Cont'd)

| | | |
|---|---|---|
| 8 | 13.7% | Cryptocrystalline Mn-rich siderite with minor quartz, chlorite, Fe(Mg) mica, jacobsite, pyrite, and trace chalcopyrite. |
| 8a | 3.9% | Fine to medium-grained Fe-rich rhodochrosite with chlorite, quartz, FeK(Mg) mica, traces of apatite, and traces of rhodochrosite. |
| 9 | 3.9% | Fine to medium-grained rhodochrosite (with minor Ca) with minor intergrown quartz and FeMn chlorite, pyrite, magnetite, and Fe oxide. |
| 10 | 2.0% | 90% mat FeMn chlorite with minor quartz, FeK(Mn) Mg mica associated with acicular hematite, and Mn oxides. |
| 11 | 2.7% | Fine to medium-grained quartz with various Mn oxides, and sometimes FeK(Mn)Mg mica and hematite masses. |
| 12 | 2.9% | Fine to coarse-grained quartz with very minor FeMn (Mg) mica, and radiating Fe(Mn) chlorite. |
| 13 | 1.0% | Light brown slate with large irregular brown "gel" blebs and fine manganite veins. |
| 14 | 1.0% | Dark grey manganiferous slate with rhodonite, braunite, ilmenite, and manganoilmenite. |
| 15 | 2.9% | Light brown/green chloritic slate with MnAlsilicate, Fe/Mn/Ti oxides, pyrite, and manganite blebs. |

** See Appendix 1 for more details.

*** See * in Table 1.

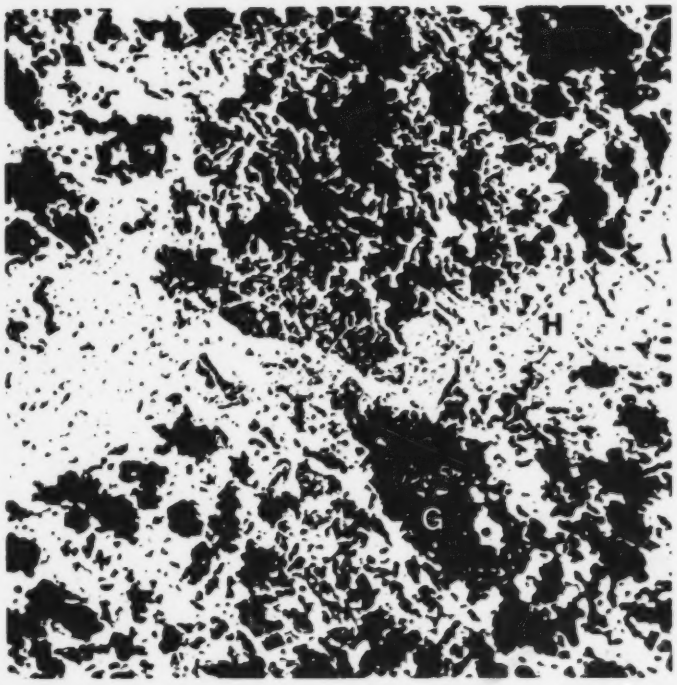
TABLE 9: Manganese-Bearing Phases in Plymouth 4 Sample

| Mineral | Ideal Formula | Relative Abundance | In Fragment Type(s): |
|---|---|---|---|
| Manganese-rich siderite | $(Fe,Mn)CO_3$ | major | 2,8 |
| Rhodochrosite (with minor Ca) | $(Mn,Ca)CO_3$ | major | 1,5,6,8a,9 |
| FeMn chlorite | $(Mg,Al,Fe,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | major | 1,6,7,9,11,12,15 |
| Iron-rich rhodochrosite | $(Mn,Fe)CO_3$ | common | 8a |
| Manganite | $MnO(OH)$ | common | 1,1a,1b,5,6,10,13,15 |
| Hausmannite | $Mn_3O_4$ | common | 5,11 |
| Pyrolusite | $MnO_2$ | trace | 5,6,11 |
| Bixbyite | $(Mn,Fe)_2O_3$ | trace | 3,4,5,13,15 |
| Jacobsite | $MnFe_2O_4$ | trace | 3,5,8 |
| Braunite | $(Mn,Si)_2O_3$ | trace | 5,14 |
| Magnetite (Mn) | $Fe_3O_4$ | trace | 6 |
| Manganoilmentite | $(Fe,Mn)TiO_3$ | trace | 14 |
| MnFeKMg mica | ? | trace | 1,14 |
| Mn(Fe,Mg)K mica | ? | trace | 3,14 |
| KFe(Mn)mica | ? | trace | 5 |
| MnTiK mica | ? | trace | 5 |
| FeAl(Mn,K,Mg) silicate | ? | trace | 6 |
| FeK(Mn)Mg mica | ? | trace | 10,11 |
| FeMn(Mg,Na)Al silicate | ? | trace | 12,13 |
| Glaucochroite | $(Ca,Mn)_2SiO_4$ | trace | 1,6 |
| Mn(Fe,Al) silicate | ? | trace | 5 |
| MnFe(Al,K) silicate | ? | trace | 5 |
| MnAl silicate | ? | trace | 15 |

medium-grained iron-rich rhodochrosite grains contains a large equant rhodochrosite (Ca) bleb approximately 40-50 micron across.

Psilomelane is another major manganese-bearing phase. It is found in a variety of forms and fragment types. Occurances of massive psilomelane with intergrown hausmannite, minor bixbyite or pyrolusite, and very minor braunite contain the largest amount of this phase (see Figure 14). Smaller amounts are found as irregular to equant blebs with rims or intergrowths of pyrolusite and thin veins approximately 1 to 10 micron wide. The blebs occur in the manganese oxide-rich fragments, 20% of the hematite-rich dark grey/red slate fragments, and 35% of the fine to medium-grained quartz with Mn oxides fragments. The veins occur in minor amounts (4%) in the Mn oxide rich fragments, 20% of the hematite-rich dark grey/red slate fragments, and one of the mat FeMn chlorite fragments.

Manganese-rich Fe chlorite, the final "major" phase, is somewhat more pervasive than the others. Generally it occurs intergrown in the 1-50 micron range with various minerals such as quartz, MnFeKMg mica, Fe Ca phosphate, FeK mica, albite, rhodochrosite (Ca), Fe chlorite, and MnAl silicate. It is found in this form in the silicified red slate with rhodochrosite fragments, some layers of the hematite-rich dark grey/red slate fragments, the very fine-grained green chloritic slate fragments with minor larger "fans", the fine to medium-grained rhodochrosite fragments, and the light brown/green chloritic slate fragments. A large amount of this chlorite also occurs as a cryptocrystalline mat with minor (~10%) medium-grained quartz, intergrown masses of FeK(Mn)Mg mica and acicular hematite, and a manganite/pyrolusite vein. Approximately 90% of these fragments is composed of the manganiferous Fe-chlorite. A small amount of this chlorite also occurs with fine to coarse-grained quartz as a fine to meidum-grained radiating mass. Iron-rich rhodochrosite, the most abundant of the "common" manganese-bearing phases, occurs in fragments as the predominant mineral. It is fine to medium-grained and intergrown with quartz, FeK(Mg) mica, Fe(Mn)




50 micron

Figure 14. Intergrown psilomelane(Ps) and hausmannite(H) with quartz, K feldspar, and minor rhodochrosite (Ca). The gangue minerals (G) are not discernable in this photograph. (Rackscatter Electron Image).

chlorite, trace apatite, and minor rhodochrosite (Ca). Large quartz grains and chlorite "fans" 5-100 micron in size are present locally.

Manganite, another common phase, occurs as thin veins 1 to 10 micron wide, irregular to equant blebs 5 to 60 micron across, and large irregular lenses. The veins are found in approximately 50% of the silicified red slate with rhodochrosite as <1% of each fragment, in the Mn oxide-rich fragments as a minor constituent, in the light brown slate with large brown "gel" blebs as a minor constituent, and in the mat chlorite fragments in trace amounts only. The blebs occur in approximately 60% of all the silicified red slate fragments often with the fine veins, in the Mn oxide-rich fragments, and in the light brown/green chloritic slate fragments. These blebs never comprise more than approximately 1 to 2% of a fragment. Generally, approximately 15% of the hematite-rich dark grey/red slate fragments contain large manganite intrusive lenses comprising approximately 10-15% of each fragment. Inclusions of acicular hematite are common.

Hausmannite is the last "common" phase. It predominantly occurs intergrown at the 1 to 10 micron level with psilomelane as large masses in the manganese oxide-rich fragments (see Figure 14). A small amount of this mineral also occurs as thin veins 1 to 10 micron across in the manganese oxide-rich fragments and the fine to medium-grained quartz. The quartz fragments also contain manganite veins, manganite blebs, and psiolomelane/pyrolusite blebs.

The remaining manganese-bearing phases occur in trace amounts only. The pyrolusite, bixbyite, and jacobsite are the most common of these. They are generally associated with other manganese oxides. For more details concerning the trace manganese minerals see Table 9 and Appendix 1.

## 4.2 General Mineralogy of the North Hartford Ore Samples

The most common manganese-bearing phases are much less consistent in the North Hartford samples than those in the Plymouth samples. However, they all do contain significant amounts of manganiferous chlorite, psilomelane, and manganite. NH1 also contains various manganese-bearing micas and MnTi oxide in relatively substantial amounts. NH2 contains a large amount of manganiferous calcite along with lesser amounts of jacobsite and pyrolusite. And, NH3 also contains a significant amount of FeMnKAl silicate. These phases are present in a great variety of forms and fragment types. The following sections describe in more detail their occurrences along with the general nature of the samples.

### 4.2.1 North Hartford 1

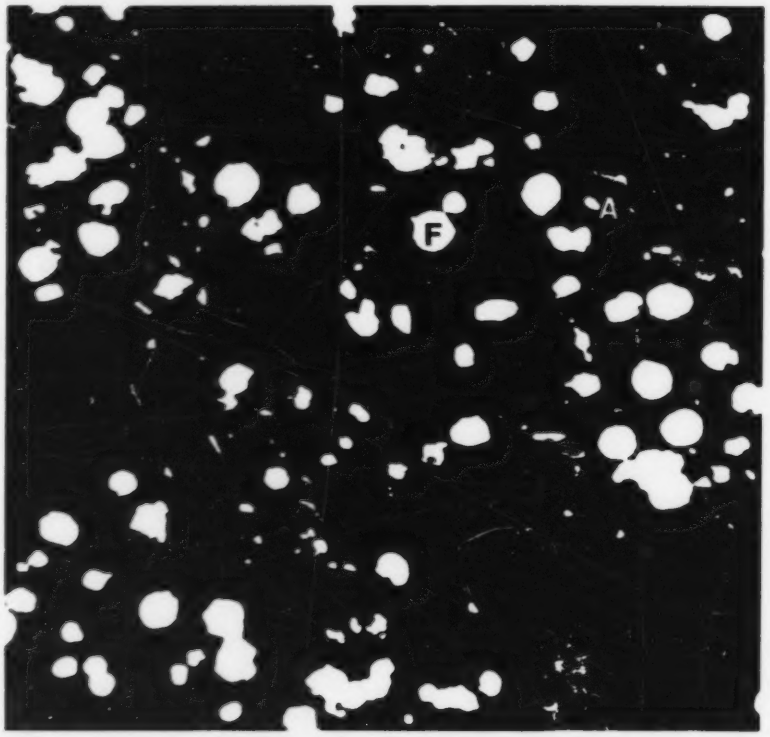
The sample population of North Hartford 1 crushed ore contains 19 fragment types. The most abundant are:

(a) Fine silicified chloritic slate with minor zircon, Ti oxide, pyrite, magnetite, pyrophanite, and very minor Mn-oxides.

(b) Somewhat coarser silicified green chloritic slate with approximately 5-30% framboidal and euhedral pyrite, minor apatite, and minor acicular pyrophanite (see Figure 15).

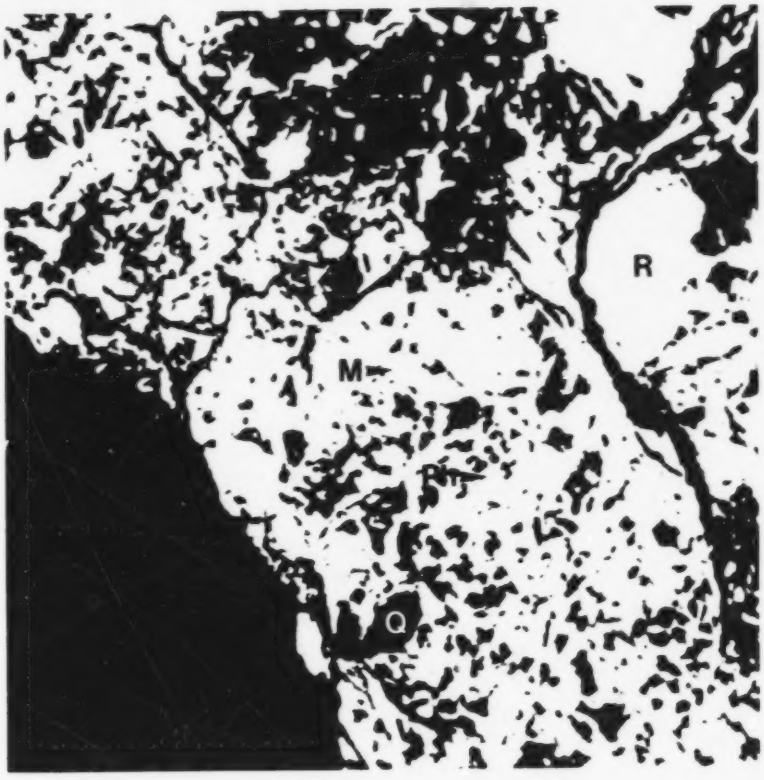
(c) Lineated and stained green chloritic slate (more manganiferous than (b)) with small amounts of Ti oxide, Fe oxide, zircon, chalcopyrite, blebby manganite, and pyrite.

(d) Rhodochrosite-bearing green chloritic slate with minor apatite, Ti oxide, Fe oxide, and framboidal pyrite (see Figure 16).




25 micron

Figure 15. Silicified green chloritic slate with bright framboidal pyrite (F) and minor apatite (A). The black material is intergrown quartz and FeK(Mg) mica. The grey patches (Ch) are composed of Fe(Mn) chlorite. (Backscatter Electron Image).




25 micron

Figure 16. Green chloritic slate containing bright rhodochrosite (R) and platey FeK(Mg) mica (Ph). The light grey interstitial material is K(Fe) mica (M) and the darkest material is quartz (Q). (Backscatter Electron Image).

(e) Red slate with minor pyrophanite, Ti oxide, hematite, Fe oxide, and secondary Mn oxides; or rhodochrosite and layered acicular to massive hematite.

These fragments make up approximately 70% of the sample. The remaining portion is comprised of various light brown, green chloritic, dark brown with acicular hematite and Fe oxide or dark grey with up to 30% Mn oxides slates; a meta-arkose with brown "gel" material; coarse to medium-grained quartz with various other phases; massive intergrown psilomelane, pyrolusite and bixbyite; and mat chlorite (see Table 10 for distribution and brief descriptions of the fragment types).

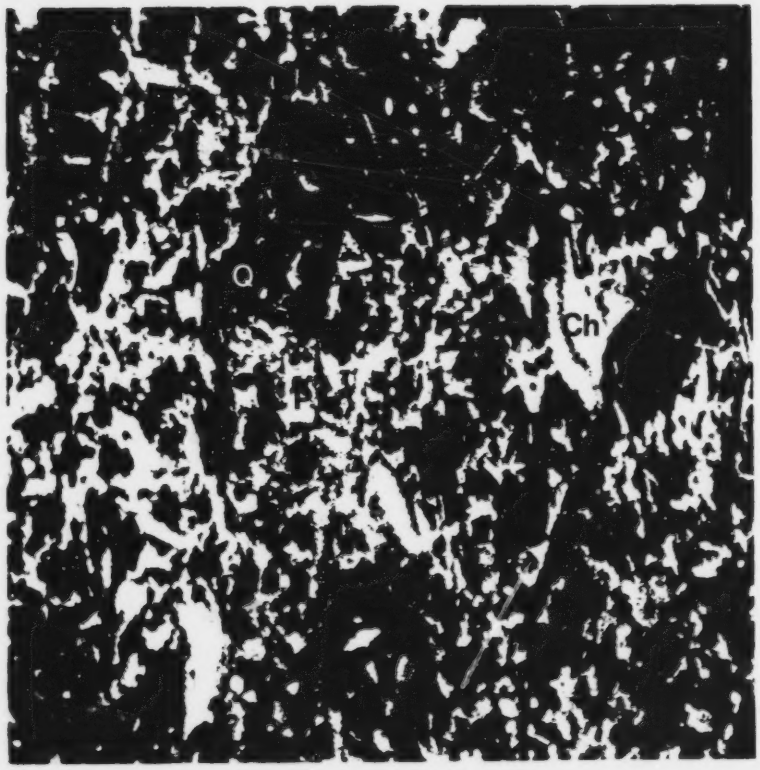
The manganese-bearing phases in these fragments are listed in Table 11 with a general estimate of their relative abundances. The common minerals are listed in approximate order of decreasing abundance.

The two major manganese-bearing phases, Fe(Mn) silicate and FeMn chlorite occur finely intergrown (1-25 micron range) with quartz, usually alkali feldspar, and a variety of mica minerals in more than half the fragment types and approximately 88% of the fragments (see Appendix A-2 for more details and Figures 17 and 18) larger "fans" of this chlorite may also be present. A single case of FeMn chlorite intergrown with Fe oxide and jacobsite as an irregular vein in medium to coarse-grained quartz is an exception. The chlorite containing only minor manganese is much more abundant than the more manganese-rich one.

The common manganese-bearing micas also occur finely intergrown with quartz, often alkali feldspar and various other micas. The MnFeK(Mg) mica occurs in the silicified green chloritic slate with 5-30% framboidal pyrite, minor apatite, and acicular pyrophanite; and in the more manganiferous yellow/green chloritic slate with minor (<1/2% of fragment) irregular pyrophanite and Ti

12.5 micron

Figure 17. Light brown/orange slate containing black quartz (Q), black K-feldspar (not discernible from quartz), light grey FeMn chlorite (Ch), white MnCaFe(K,Mg)AlP silicate or KFe(Mg) mica (A), and minor Fe oxide or Ti oxide (O). (Backscatter Electron Image).



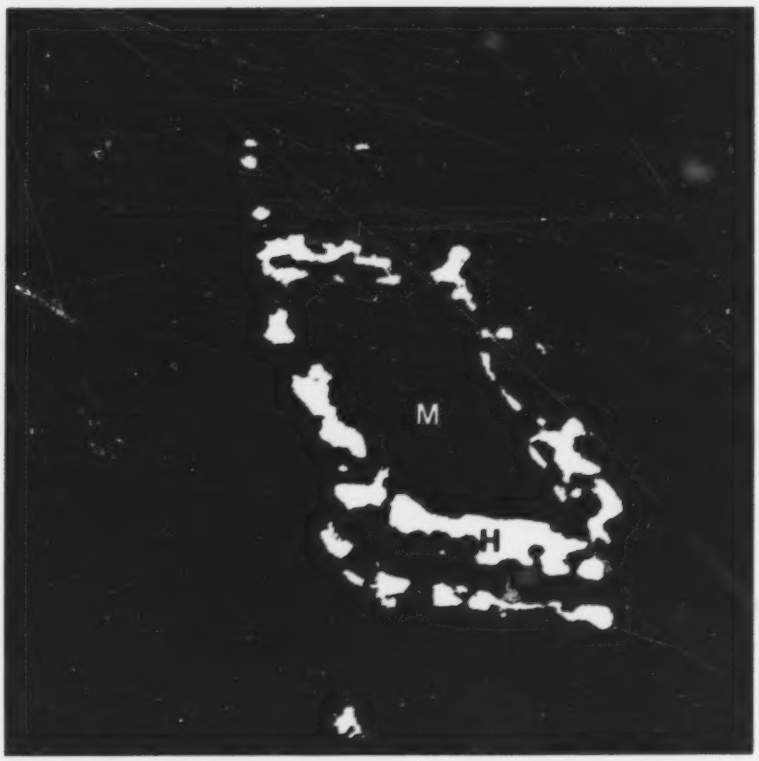

25 micron

Figure 18. Yellow/green chloritic slate with minor pyrophanite (P) and Ti oxide (T). The very darkest grey material (Q) is quartz and albite. The slightly lighter material is FeMnK(Mg) mica (Ph) and the lightest grey material is FeMn chlorite (Ch). (Backscatter Electron Image).

oxide (see Figure 18). The Fe(Mn,Ti)KMg mica is found in the lineated and stained green chloritic slate along with the Fe(MnMg)K mica. The FeTi(Mn,K)Mg chlorite occurs in the more abundant fine silicified chloritic slate with FeK(Mg)Al silicate and FeKMg mica. Finally, the Fe(Mn,Mg)K mica also occurs in the red slate often with minor Fe chlorite and quartz.

The pyrophanite occurs in small amounts (usually less than 1%) as irregular elongate or acicular grains 1 to 10 microns long scattered in various green, light brown, and red slates (see Table 11 for specific fragment types). In one case the pyrophanite occurs as a middle layer of a thick (40-60 micron wide) vein between the magnetite core and the "wispy" psilomelane rim. This vein occurs in the fine silicified green chloritic slate.

Both manganite and psilomelane are much less abundant than the other "common" minerals. The manganite occurs as thin (1-5 micron) veins with minor pyrolusite or hausmannite in the dark silicified slate. This fragment type also often contains 2-20% small (10-25 micron across) equant manganite blebs with local psilomelane inclusions. Similar blebs or thin veins occur in 25% of the fragments of red slate with minor Mn/Ti/Fe oxides. Equant manganite blebs (10-35 micron across) also occur in one fragment of fine silicified green chloritic slate along with a 10-25 micron wide pyrolusite and psilomelane vein; and in one fragment of lineated and stained green chloritic slate. Finally, an unusual occurrence of manganite is present in the dark silicified slate mentioned above. Braunite crystals have been altered to alternating layers of manganite and hausmannite (see Figure 19).




5 micron

Figure 19. Layered manganite (M) and hausmannite (H) pseudomorph after braunite in the dark secondary manganese oxide-rich slate. (Backscatter Electron Image).

TABLE 10: Distribution and Brief Description of Fragment Types in Sample NH1.

| Fragment Type | Percentage of Sample Population* | Brief Description** |
|---|---|---|
| 1 | 12.4% | Silicified green chloritic slate with 5-30% framboidal pyrite. |
| 2 | 29.8% | Fine silicified green chloritic slate with minor amounts of Ti oxide, pyrite and secondary Mn-oxides. |
| 2a | 10.2% | Lineated and stained green chloritic slate with various scattered oxides and sulfides. |
| 3 | 5.8% | Meta-arkose with minor Ti oxide and 10-20% brown "gel" material. |
| 4 | 4.3% | Light brown/orange slate with minor Fe oxide, Ti oxide and often MnCaFe(K,Mg)AlP Silicates. |
| 5 | 0.7% | Green chloritic meta-greywacke with minor apatite. |
| 6 | 2.2% | Dark brown silicified slate with acicular hematite and anhedral Fe oxide. |
| 7 | 5.1% | Yellow/green (manganiferous) chloritic slate with minor pyrophanite and Ti oxide. |
| 8 | 8.0% | Rhodochrosite-bearing green chloritic slate with rare Ti oxide, Fe oxide, and framboidal pyrite. |

TABLE 10 (Cont'd)

| | | |
|---|---|---|
| 9 | 6.5% | Dark silicified slate with up to approximately 30% secondary Mn oxides. |
| 10 | 1.4% | Medium to coarse-grained quartz with minor FeMn chlorite, Fe oxide, and jacobsite in irregular veins. |
| 11 | 0.7% | Three layers of chloritic slates of varying coarseness. |
| 12 | 8.0% | Red slate with minor Mn/Ti/Fe oxides, and secondary Mn-oxides. |
| 13 | 1.4% | Red slate with layered acicular to massive hematite, and rhodochrosite. |
| 14 | 0.7% | Light brown silicified slate with minor apatite, pyrophanite, and hematite. |
| 15 | 0.7% | Dark silicified slate with approximately 2% euhedral magnetite, Fe oxide, acicular hematite and minor pyrite. |
| 16 | 0.7% | 35% massive intergrown psilomelane, pyrolusite, and bixbyite, with fine to medium-grained quartz and tephroite. |
| 17 | 0.7% | Light brown slate with manganoilmenite, hematite, and pyrophanite. |
| 18 | 0.7% | Fine to medium-grained mat chlorite. |

*** See * in Table 1.

** See Appendix A-2 for more details.

TABLE 11 Manganese-Bearing Phases in North Hartford 1 Sample

| Mineral | Ideal Formula | Relative Abundance | In Fragment Type(s): |
|---|---|---|---|
| Fe(Mn) Chlorite | $(Mg,Al,Fe,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | major | 1,2,2a,8,9,15 |
| FeMn Chlorite | $(Mg,Al,Fe,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | major | 4,6,7,10,11,13 |
| MnFeK(Mg) mica | ? | common | 1,7 |
| Fe(Mn,Ti)KMg mica | ? | common | 2a |
| FeTi(Mn,K)Mg chlorite | $(Mg,Al,Fe,Ti,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | common | 2 |
| Fe(Mn,Mg)K mica | ? | common | 2a,12 |
| Pyrophanite | $MnTiO_3$ | common | 1,2,12,14,17 |
| Manganite | $MnO(OH)$ | common | 2,2a,9,12 |
| Psilomelane | hard manganese oxides | common | 2,9,12,16 |
| Pyrolusite | $MnO_2$ | trace | 2,9,12,16 |
| Hausmannite | $Mn_3O_4$ | trace | 9 |
| Jacobsite | $MnFe_2O_4$ | trace | 10,12 |
| Bixbyite | $(Mn,Fe)_2O_3$ | trace | 16 |
| Manganoilmenite | $(Fe,Mn)TiO_3$ | trace | 17 |
| Rhodochrosite | $MnCO_3$ | trace | 8 |
| Fe(Ca)-rich Rhodochrosite | $(Mn,Fe)CO_3$ | trace | 13 |
| MnCaFe(MgAl,P) Silicate | ? | trace | 4 |
| MnFe(Ca,K)Al Silicate | ? | trace | 13 |
| Tephroite | $Mn_2[SiO_4]$ | trace | 16 |

The psilomelane occurs in various forms. Those in the fine silicified green chloritic slate, and the dark silicified slate are described in the previous two paragraphs. Along with these, the psilomelane is found as a massive intergrowth (5-25 micron range) with a smaller amount of pyrolusite and blocky bixbyite. And, in one fragment of red slate with minor Mn/Ti/Fe oxides, a large (35-60 micron wide) vein contains a layer of psilomelane between the pyrolusite core and jacobsite rim.

The remaining manganese-bearing phases listed in Table 11 are present in trace amounts only. Some of their occurrence have been mentioned above; however, for more details on all of them see Appendix A-2.

### 4.2.2 North Hartford 2

The sample population from the North Hartford 2 crushed ore contains 15 fragment types. The most abundant of these are:

(a) A silicified light brown/green slate containing minor albite, calcite, Ti oxide, ilmenite, pyrite, and Fe oxide frequently (25% of fragments) with secondary Mn/Fe oxides in equant bleb and vein forms.

(b) A very silicified green/light brown chloritic meta-greywacke containing 50-80% quartz, often large chlorite "fans", minor Ti oxide, Fe oxide, minor pyrite, and infrequently secondary Mn oxides.

(c) Fragments of 20-80% fine to medium-grained calcite (Mn) coarsely intergrown (25-125 micron range) with a variety of minerals such as quartz, albite, Fe chlorite and K(FeMg) mica and containing minor framboidal pyrite, Ti oxide, Fe oxide, and in one fragment minor equant blebs of psilomelane.

(d) A silicified slatey material with abundant (approximately 15-55%) secondary Mn/Fe oxides in a variety of forms from small equant blebs to large blocky veins.

These fragment types make up approximately 80% of the sample population. The remaining fragments consist of stained mat chlorite predominantly fine or coarse-grained quartz with various other phases, massive secondary manganese oxides, dark grey hematite-rich or silicified red slate, and stained meta-greywacke or arkose. Table 12 contains more details on the distribution and descriptions of all the fragment types.

This sample contains a large number of manganese-bearing phases as listed (with the fragment types they are found in) in Table 13. The major and common minerals are listed in order of abundance, although the relative amounts do not vary a great deal.

The calcite (Mn), however, is definitely the most abundant of these phases. It occurs primarily as fine to medium-grained material comprising 20-80% (usually approximately 55-65%) of the fragment. It is coarsely intergrown with quartz, alkali feldspar, and minor chlorite or K(Fe,Mg) mica. Traces of framboidal pyrite (as much as 1% in one fragment), psilomelane blebs, irregular Ti oxide (2-5 micron long) and Fe oxide sometimes coating pyrite may also be present. Also, 5% of the silicified light brown/green slate also contains this phase finely intergrown (1-20 micron range) with quartz, Fe(Mn) chlorite, KFe(Mg) mica, and albite.

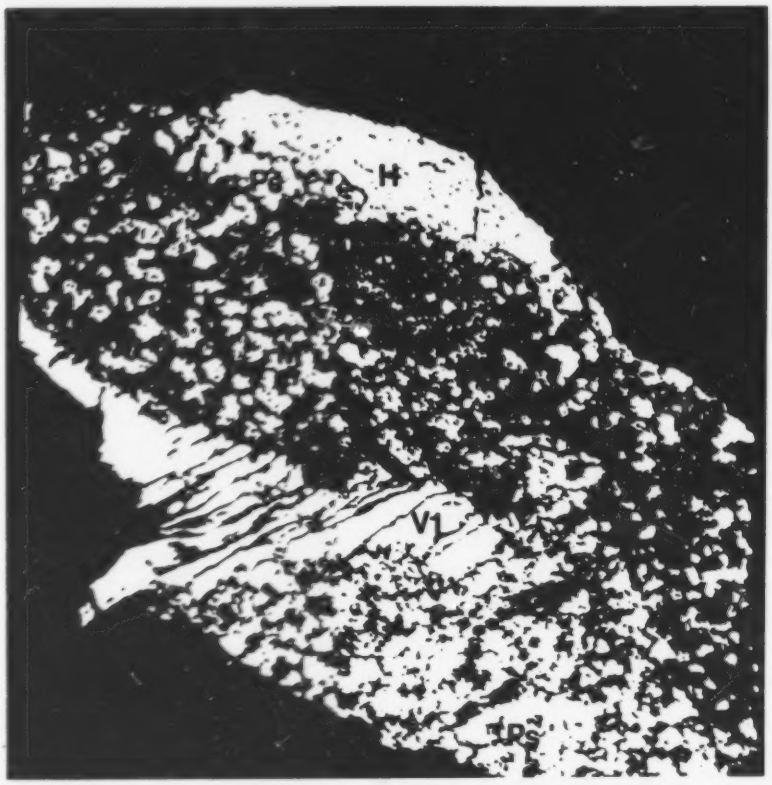
The secondary Mn/Fe oxides comprise most of the common manganese-bearing phases, the only exception is Fe(Mn) chlorite. It most commonly occurs intergrown with quartz and KFe mica in the very silicified green/light brown meta-greywacke. Minor Ti oxide, Fe oxide, pyrite, manganite as irregular blebs, and psilomelane as irregular blebs or, in one case, as a thick vein (approximately 60 micron wide) are scattered through these fragments. A small

number of fragments predominantly composed of a mat of medium-grained "feathery" Fe(Mn) chlorite have also been observed. They contain minor intergrown albite, Fe chlorite, and K(Fe) mica small masses. Intergrown jacobsite, and psilomelane/bixbyite blebs and one vein approximately 40 micron wide have also been observed. Finally, Fe(Mn) chlorite occurs finely intergrown with FeMg(Al,Mn) silicate, minor apatite, FeK(Mg) mica, and 20-50% irregular to acicular hematite in dark grey chloritic slate fragments. Irregular blebs of intergrown manganite and psilomelane intrude on this assemblage.

Manganite, the most abundant of the manganese oxides, occurs in a variety of forms and fragment types. Most commonly it forms irregular to equant blebs (10-70 micron across) found in one fragment of the very silicified green/light brown greywacke, in approximately 10% of the silicified light brown/green slate (see Figure 20), in all the stained meta-greywacke fragments (with intergrown 3-10 micron range jacobsite), and in more than 50% of the rich dark slatey material often with blebs of other manganese oxides (see Figure 21). These blebs never comprise more than approximately 10% of the fragment. The silicified light brown/green slate also contains one example of a large intergrown manganite pyrolusite vein (see Figure 20) and can contain up to 15% small (1-10 micron wide) veins often with psilomelane. The manganite also occurs as minor intergrowths or large masses (200-500 micron across) in massive psilomelane with minor pyrolusite, hematite and no more than 15% gangue material. Similar intergrown manganite/psilomelane masses intrude in the hematite-rich dark grey chloritic slate. Intergranular masses and irregular veins of manganite with minor pyrolusite, jacobsite and

50 micron

Figure 20. Silicified light brown/green slate with a large manganite/pyrolusite "vein" (V1), small manganite blebs (M), larger and more irregular jacobsite blebs (J), and manganite/Fe(Mn)KMg mica veins (V2). The white material in these veins is the manganite. The very darkest grey material is quartz (Q). The slightly lighter material (Ch) is Fe chlorite and KFe(Mg) mica. (Backscatter Electron Image).




125 micron

Figure 21. A fragment of manganese oxide-rich silicified slatey material containing a large psilomelane/minor pyrolusite vein (V1), irregular psilomelane blebs with pyrolusite rims (Ps), manganite blebs (M), and hematite (H). The dark material is intergrown Mn(Fe)Ca(P, Al) silicate, quartz, and MnCa silicate. (Backscatter Electron Image).

TABLE 12: Distribution and Brief Description of Fragment Types in Sample NH1.

| Fragment Type | Percentage of Sample Population* | Brief Description** |
|---|---|---|
| 1 | 24.0% | Very silicified green/light brown meta-greywacke with Ti oxide, Fe oxide, pyrite, and various secondary Mn oxides. |
| 2 | 1.6% | Stained mat Fe(Mn) chlorite with minor secondary Mn/Fe oxides, albite, Fe chlorite, and K(Fe) mica. |
| 3 | 1.6% | Coarse-grained quartz with very minor Mn(Fe) chlorite inclusions. |
| 4 | 33.4% | Silicified light brown/green slate with minor calcite, Fe/Ti oxides, pyrite, and secondary Mn/Fe oxides. |
| 5 | 1.6% | Stained meta-greywacke with 5-10% Ti/Mn/Fe oxides, and manganite/jacobsite blebs. |
| 6 | 3.9% | Massive secondary Mn oxides with 3-15% rhodochrosite and various manganiferous micas. |
| 7 | 10.7% | 20-80% calcite with quartz, albite, Fe chlorite, K(FeMg) mica, pyrite, and various Mn/Fe/Ti oxides. |
| 8 | 10.2% | Silicified slatey material with various secondary Mn/Fe oxides, hematite, and minor magnetite. |

TABLE 12 (Cont'd)

| | | |
|---|---|---|
| 9 | 3.0% | Silicified arkose with minor Ti oxide, Fe oxide, psilomelane, and pyrolusite. |
| 10 | 3.0% | Dark grey chloritic slate with 20-50% fine irregular or acicular hematite and secondary Mn oxides. |
| 11 | 1.6% | 65-75% calcite (Mn) with coarsely intergrown quartz and alkali feldspar. |
| 12 | 0.8% | Medium to fine-grained CaTiAl silicate, Fe chlorite, albite, K(Mg) mica, and CaFeMgAl Silicate. |
| 13 | 3.0% | Red silicified slate with minor Ti/Fe/Mn oxides. |
| 14 | 0.8% | Coarsely smeared silica with long "feathery" grains of chlorite. |
| 16 | 0.8% | Stained finely intergrown quartz, K(Fe,Mg) mica, and minor MnFe chlorite with trace Ti oxide. |

***See * in Table 1.

**See Appendix 3 for more details.

TABLE 13: Manganese-Bearing Phases in North Hartford 2 Sample

| Mineral | Ideal Formula | Relative Abundance | In Fragment Type(s): |
|---|---|---|---|
| Calcite (Mn) | $CaCO_3$ | major | 4,7,11 |
| Manganite | MnO(OH) | common | 1,4,5,6,8,10 |
| Fe(Mn) Chlorite | $(Mg,Al,Fe,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | common | 1,2,10 |
| Psilomelane | hard manganese oxides | common | 1,2,4,6,7,8,9.10 |
| Pyrolusite | $MnO_2$ | common | 4,6,8,9 |
| Jacobsite | $MnFe_2O_4$ | common | 2,4,5,8 |
| Bixbyite | $(Mn,Fe)_2O_3$ | trace | 2,8 |
| Manganoilmenite | $(Fe,Mn)TiO_3$ | trace | 13 |
| Ti(Mn,Fe) oxide | ? | trace | 5 |
| Mn(Fe) chlorite | $(Mg,Al,Mn,Fe)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | trace | 3 |
| Fe(Mn) chlorite | $(Mg,Al,Mn,Fe)_{12}[(Si,Al)_{O20}](OH)_{16}$ | trace | 8,16 |
| Fe(Mn)KMg mica | ? | trace | 1,4 |
| MnKAl Silicate | ? | trace | 6 |
| MnFe(Ti,Mg)Al garnet | $(Mn,Fe,Mg)_3Al_2Si_3O_{12}$ | trace | 6,8 |
| Rhodochrosite (minor Ca) | $MnCO_3$ | trace | 6 |
| Mn(K,Ca)Al Silicate | ? | trace | 8 |
| Glaucochroite | $(Ca,Mn)_2SiO_4$ | trace | 8 |
| Mn(Fe)Ca(P,Al) Silicate | ? | trace | 8 |

bixbyite have also been observed in fine to medium-grained quartz, comprising 30-60% of the fragment. Finally, one fragment of the manganese oxide-rich dark slatey material contains veins of manganite, jacobsite and, as the rim, Mn(K,Ca)Al silicate (See Figure 23).

Psilomelane is another common manganese oxide. Several of its occurrences have been mentioned previously. The most common form for this phase is as irregular to equant blebs from 5 to 50 micron across. They occur with intergrown pyrolusite in the silicified arkose; with intergrowths or rims of pyrolusite in the manganese oxide-rich silicified slatey material (see Figure 21); with intergrowths or rims of pyrolusite in the manganese oxide-rich silicified slatey material; as less than 1/2% of the 20-80% calcite fragments; <10 micron across in the silicified light brown/green slate; with minor bixbyite in the stained mat chlorite; and <10 micron across in one fragment of the very silicified green/light brown greywacke. The latter 3 fragment types also contain fine (1-5 micron wide) or thick (40-60 micron wide) veins often with bixbyite or manganite. Large veins 5-30 micron wide of pyrolusite and/or psilomelane have also been observed in the manganese oxide-rich silicified slatey material (see Figure 21) and in the massive psilomelane, manganite, and often pyrolusite intergrowths mentioned in the previous paragraph.

The occurrences of the last two common manganese-bearing phases, pyrolusite and jacobsite, have basically been discussed in previous paragraphs; however there are 3 cases still unexplained. Along with various associations with manganite and psilomelane, the pyrolusite occurs as thin veins 5-15 micron wide in 33% of the fragments containing massive secondary psilomelane, pyrolusite, and manganite. The jacobsite, along with its manganite associations, occurs in the mat chlorite as fine intergranular material and in one fragment of the silicified light brown/green slate as subequant blebs. All the other associations are similarly minor compared to the manganite and psilomelane.

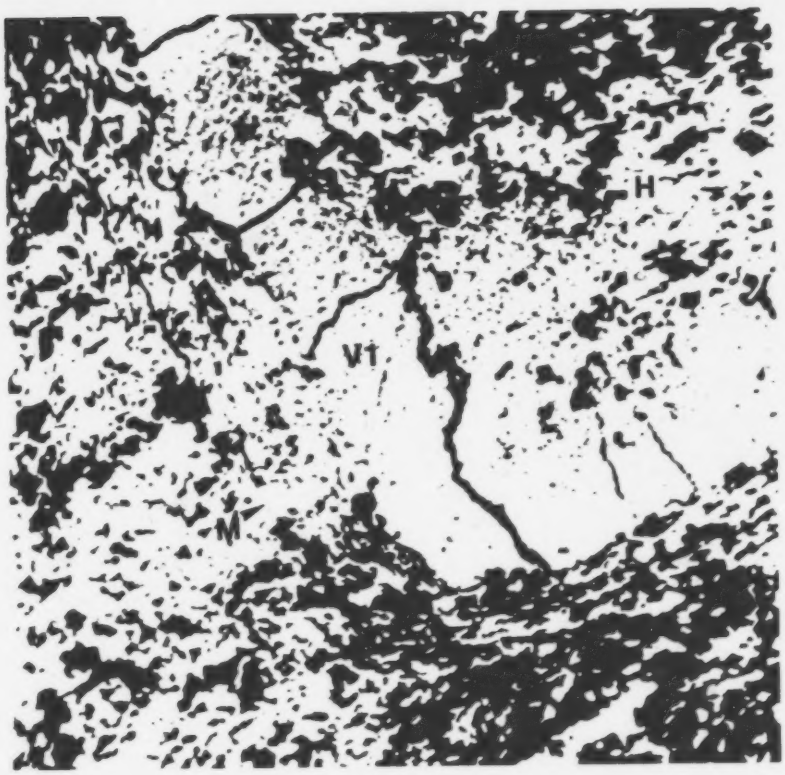



Figure 22. Manganese oxide-rich slatey material with a large blocky psilomelane vein (V1). The white acicular grains (H) are hematite crystals and the anhedral grey material intergrown with them is manganite (M). The black gangue minerals are quartz and Fe(Mn, Mg)K mica. The unseen portions of this fragment contains only traces of hematite, but much manganite in large irregular blebs. (Backscatter Electron Image).

The remaining manganese-bearing phases occur in much smaller amounts and thus have been designated as "trace" minerals. Many of their occurrences have been described above. For more details on all of these trace phases see Table 13 and Appendix A-2.

4.2.3 North Hartford 3

The sample population of the North Hartford 3 crushed ore is comprised of 15 fragment types. The most common are:

(a) Green/brown chloritic slate comprised of finely intergrown quartz, Fe(Mn) chlorite, KFe(Mg) mica and KFeMg mica with <1/2% of irregular Ti oxide grains, minor subhedral to eudral pyrite and Fe oxide, and often various secondary Mn/Ti oxides.

(b) Brown/green silicified chloritic arkose with large subrounded quartz and albite grains surrounded by a cement/matrix of Fe(Mn) chlorite, KFeMg mica, FeKMg mica, and quartz with trace amounts of apatite, ilmenite, Ti oxide, Fe oxide, zircon, and, in one case, blebs of manganite.

(c) Brown silicified chloritic arkose, not manganiferous except for minor jacobsite grains, with large veins or blebs of hematite and magnetite, minor zircon, minor Ti oxide, and minor Fe oxide.

(d) Very fine-grained, unalligned quartz, K(Fe, Mg) mica and trace Fe(Mn)KMg mica with <1/2% small irregular grains of Ti oxide.

These types make up approximately 75% of the sample population. The remaining fragments are comprised of various light coloured slates, red hematite/magnetite/psilomelane-rich slate, hematite-rich dark grey slate, quartz sandstone, manganite-rich fragments, and fine to medium-grained quartz with various intergrown minerals such as albite and chlorite (see Table 14 for distribution and brief descriptions of the fragments).

Table 15 lists the manganese-bearing phases found in this sample along with a very general estimate of their relative abundances and the fragment types they are contained in. The

"major" and "common" minerals are listed in order of decreasing abundance.

TABLE 14: Distribution and Brief Description of Fragment Types in Sample NH3.

| Fragment Type | Percentage of Sample Population*** | Brief Description** |
|---|---|---|
| 1 | 11.4% | Brown/green silicified chloritic arkose with minor amounts of various Fe/Ti oxides and minor secondary manganite. |
| 2 | 2.6% | Fine to medium grained intergrown quartz, "smeared" potassium feldspar, and Fe(Mn) chlorite with Fe and Ti oxides. |
| 3 | 3.5% | Very silicified chloritic slate with minor Fe/Ti oxides and secondary Mn oxides. |
| 4 | 1.8% | Fine-grained quartz and albite with minor alligned chlorite and K(Fe) mica, and minor Fe/Ti oxides. |
| 5 | 47.2% | Green/brown chloritic slate, somewhat silicified with Fe/Ti oxides, minor pyrite, and various secondary Mn/Fe oxides. |
| 6 | 0.9% | Red slate with irregular grains of hematite, magnetite, and psilomelane. |
| 7 | 4.4% | Fine-grained silica with minor albite, K(Mg, Fe) mica, chlorite, and various Fe/Ti oxides. |
| 8 | 3.5% | Dark grey silicified slate with acicular to irregular hematite and minor amounts of various Mn oxides. |
| 9 | 1.8% | Fine to medium grained quartz and minor albite with small amounts of chlorite and fine Fe/Ti oxides. |

TABLE 14 (Cont'd)

| | | |
|---|---|---|
| 10 | 7.9% | Brown silicified chloritic arkose, similar to type 1 but less manganiferous and chloritic. |
| 11 | 7.9% | Very fine-grained quartz, K(Fe, Mg) mica and Fe(Mn)KMg mica with minor Ti oxide - no allignment of the micas. |
| 12 | 2.6% | Manganite-rich fragments with interstitial quartz, FeMnK mica, and albite along with minor hematite and pyrolusite. |
| 13 | 0.9% | Silicified, unalligned Type 5 slate with minor apatite and Fe/Ti oxides. |
| 14 | 1.8% | Light grey silicified slate with minor Ti/Fe oxides. |
| 15 | 1.8% | Coarse-grained quartz sandstone with a highly silicified and chloritized cement/matrix. |

** See Appendix A-2 for more details.

*** See * of Table 1.

TABLE 15: Manganese-Bearing Phases in North Hartford 3 Sample

| Mineral | Ideal Formula | Relative Abundance | In Fragment Type(s): |
|---|---|---|---|
| Fe(Mn)chlorite | $(Mg,Al,Fe,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | major | 1,2,5,8,13 |
| Manganite | MnO(OH) | common | 1,3,5,8,12 |
| Psilomelane | hard manganese oxides | common | 1,3,6,8 |
| FeMnK mica | ? | common | 12 |
| Pyrolusite | $MnO_2$ | trace | 12 |
| Jacobsite | $MnFe_2O_3$ | trace | 5,10 |
| Magnetite (Mn) | $Fe_3O_4$ | trace | 6 |
| MnFe chlorite | $(Mg,Al,Fe,Mn)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ | trace | 4 |
| KFe(Mn)Mg mica | ? | trace | 8 |
| FeK(Mn)Mg mica | ? | trace | 11 |

Chlorite with minor manganese, is the most pervasive of all the manganese-bearing phases. It generally occurs finely intergrown at anywhere from 5-50 micron with quartz, alkali feldspar, often trace apatite, and KFe(Mg) mica, KFeMg mica, FeK mica, KFe(Mn)Mg mica or K(Fe) mica in various fragment types. Fe/Ti oxides and often secondary Mn/Fe oxides are also present. Large "fans" from 30 to 100 micron long have been observed in the brown/green silicified arkose and the green/brown chloritic slate.

Manganite, the most abundant of the manganese oxides, occurs as thin veins (1-5 microns wide) and small irregular to equant blebs (1-15 microns across) in various fragment types. The thin veins are found in approximately 25% of the very silicified chloritic slate, in approximately 5% of the very abundant green/brown chloritic slate, and in approximately 25% of the hematite-rich dark grey silicified slate. They never comprise more than about 2% of a fragment. The irregular to equant blebs occur in approximately 10% of the brown/green silicified arkose, as traces in 2% of the very abundant green/brown chloritic slate, as 1-2% of each fragment in 25% of the hematite-rich dark grey silicified slate, and as 10-30% of the manganite-rich silicifed slate (see Figure 23). Locally the blebs are associated with other manganese oxides, but they generally do not contain inclusions of these minerals.

Psilomelane, the other common manganese-oxide, occurs as larger often blocky veins (2-20 micron wide) and irregular to equant blebs (5-60 micron across) in basically the same fragment types as the manganite. The veins occur in approximately 4% of the abundant green/brown chloritic slate, and in approximately 25% of the hematite-rich dark grey silicified slate with large psilomelane blebs. They too never comprise more than approximately 2% of any fragment. The blebs are present in 25% of the very silicified chloritic slate as traces, in the red slate as intergranular grains with hematite (see Figure 24), and in 75% of the hematite-rich dark grey silicified slate as subequant forms

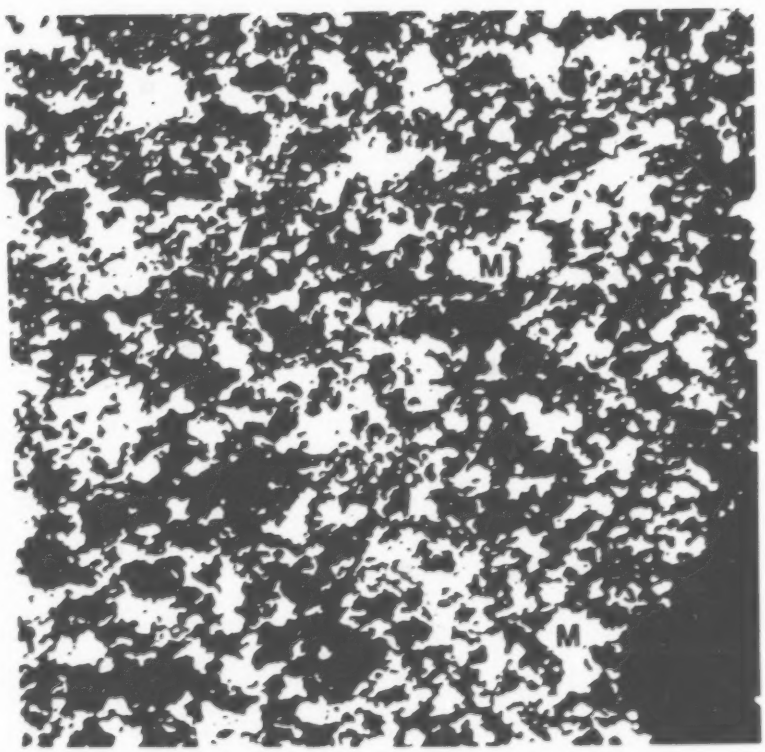
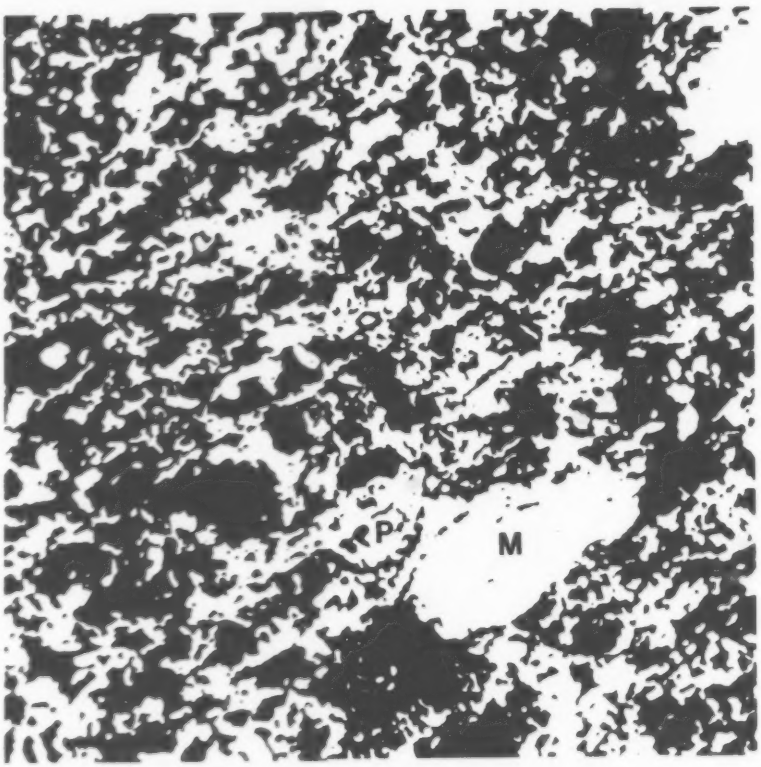



Figure 23. Manganite-rich slate with dark interstitial quartz, albite, and FeMnK mica. Irregular to equant manganite blebs (M) and minor hematite (not discernable from the manganite although it is part of the finer bright material) comprise a large part of this fragment. (Backscatter Electron Image)



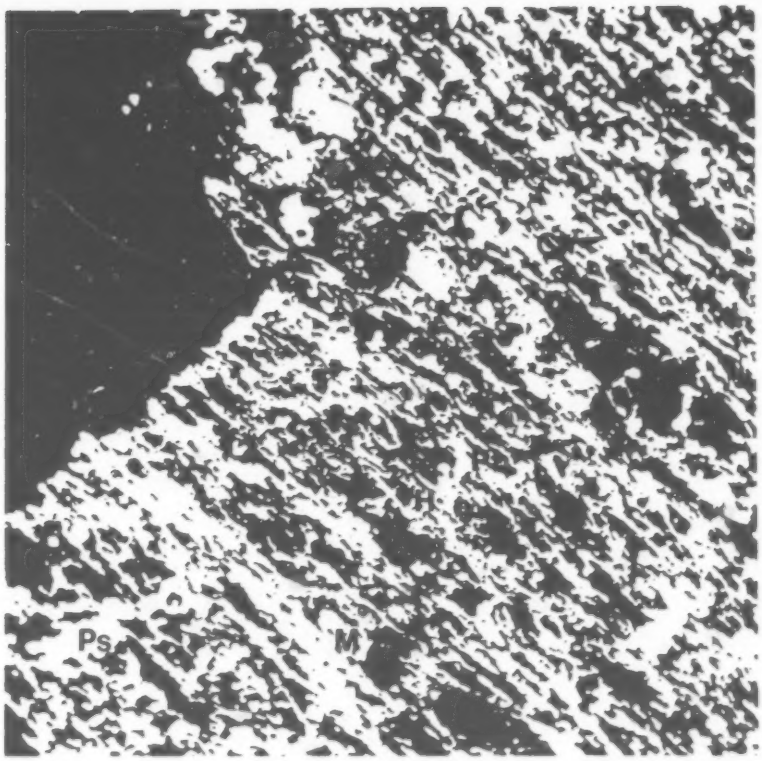

25 micron

Figure 24. Red slate with irregular grains of hematite (H) and psilomelane (P). The hematite is difficult to discern from the psilomelane; however, it is somewhat more angular in this photograph. The large bright grain is magnetite (M). The dark material is large albite grains and intergrown KFe mica. (Backscatter Electron Image).

often with manganite blebs (see Figure 25) or as narrow elongate lenses intergrown with the hematite and gangue. These blebs never comprise more than approximately 5% of a fragment.

The final "common" phase is FeMnK mica. It occurs finely intergrown at the 2-8 micron range with quartz and albite in the manganite-rich slate containing minor hematite and pyrolusite (in the manganite blebs). This mica comprises approximately 25-35% of each fragment.

The remaining manganese-bearing phases present in this sample occur in trace amounts. For details on their occurances see Table 15 and Appendix A-2.




50 micron

Figure 25. Dark grey silicified slatey material with fine elongate hematite (H), irregular psilomelane blebs (Ps), and smaller irregular manganite blebs (M). The darkest material is quartz and albite. The dark grey material is K(Fe, Mg) mica (Ph), and some of the bright grey white elongate grains are MnFe chlorite (Ch) not hematite. They are not distinct in this photograph. (Rackscatter Electron Image).

## 5.0 CONCLUSIONS

Small amounts of homogenized crushed ore from a series of samples of material from the Plymouth and North Hartford deposits were examined. In each sample the petrology and mineralogy is quite variable. The manganese-bearing minerals made up a large portion of the Plymouth samples (except sample P5) and a much smaller portion of the North Hartford samples. A great variety of mineral types occurred in both deposits. The most common of these are as follows:

(a) Plymouth Deposit:
- Manganese-rich carbonates
- Manganiferous chlorite
- Mn(K)Al silicate
- Braunite
- Manganite
- Psilomelane
- Hausmannite
- Pyrolusite

(b) North Hartford Deposit:
- Manganiferous calcite
- Manganiferous chlorite
- Manganite
- Psilomelane
- Pyrolusite
- Jacobsite
- MnFeK(Mg) mica
- Fe(Mn,Ti)Mg mica
- FeTi(Mn,K)Mg mica
- Pyrophanite

See Table 16 for details on the distribution of these minerals in each sample.

TABLE 16: A summary of the major and common minerals for samples studied. The information is taken from Tables 3, 5, 7, 9, 11 and 13.

PLYMOUTH DEPOSIT

Major Minerals

| Sample P-1 | P-2 | P-3 | P-4 |
|---|---|---|---|
| Rhodochrosite (Ca) | Braunite | Manganite | Siderite (Mn) |
| Braunite | Mn chlorite | Rhodochoriste | Rhodochrosite (Ca) |
| Fe (Mn) Chlorite | | Psilomelane | FeMn chlorite |

Common Minerals

| | | | |
|---|---|---|---|
| Psilomelane (Ca) | Manganite | Fe (Mn) Chlorite | Rhodochrosite (Fe) |
| Pyrolusite | Psilomelane | Hausmannite | Manganite |
| Manganite | Mn (K) Al silicate | Pyrolusite | Hausmannite |
| | Rhodochoriste | | |
| | Pyrolusite | | |

NORTH HARTFORD DEPOSIT

Major Minerals

| Sample NH-1 | NH-2 | NH-3 |
|---|---|---|
| Fe (Mn) Chlorite | Calcite (Mn) | Fe (Mn) chlorite |

Common Minerals

| | | |
|---|---|---|
| FeMn Chlorite | Manganite | Manganite |
| MnFeK (Mg) mica | Fe (Mn) Chlorite | Psilomelane |
| Fe (Mn, Ti) KMg mica | Psilomelane | FeMnK mica |
| FeTi (Mn, K) Mg chlorite | Pyrolusite | |
| Fe (Mn, Mg) K mica | Jacobsite | |
| Pyrophanite | | |
| Manganite | | |
| Psilomelane | | |

The manganese-bearing minerals are also very fine-grained usually (less than 50 microns) and intergrown with other manganese-poor minerals. In general, the common micas, chlorites, and the Mn(K)Al silicate occur finely intergrown with the other minerals contained in the various slates of the deposits. The braunite, found only in the Plymouth sample, occurs as spherulitic to massive aggregates. The manganiferous carbonates are commonly found as fine to coarse-grained aggregates intergrown with other phases which comprise as much as 30% of a manganiferous carbonate-bearing fragment. The Mn/Fe oxides appear to be secondary. They occur as small irregular to equant blebs, thin and thick veins, and large blocky masses. The manganese-bearing minerals that are found in trace amounts only generally occur in the same manner as the common phases mentioned above.

The nature of these deposits creates serious processing problems. Physical separation of manganese phases would be extremely difficult because most of the material is very finely intergrown - the longest dimensions not exceeding 50 micron and often being less than 25 micron. Chemical separation is complicated by the great variety of mineral types containing manganese. A single leaching process probably would not recover the manganese from all mineral types and recovery efficiency would vary for those mineral types affected. Finally, a significant amount of manganese, that which occurs as a minor component of such minerals as chlorite and the micas, may not be recovered by either method. All these facts seem to indicate that it would be very difficult to produce high grade concentrates from the material of these deposits.

## 6.0 RECOMMENDATIONS

Very little work on the mineralogy of the Plymouth and North Hartford deposits has been done. This study has examined only a small amount of crushed material from each deposit. Because of the great variability found in the petrology and manganese-mineralogy of the material examined and the small amount of material, the samples may not be good representations of the deposits. In fact, only very small amounts manganese-bearing phases were found in the North Hartford samples, much less than expected. To confirm or revise this study, further examination of the deposits is recommended.

If, for this reason, further examination is decided upon, a more detailed deposit study, one in which selected sampling was done, would be advisable. The results would confirm or correct this study and, furthermore, give a more accurate view of the extent of the manganese enrichment (notice the lack of significant manganese in sample P5), and the positions and extent of the various phases from which the manganese is recoverable. All this would aid in the recovery and, to some extent, processing of the ore in the two deposits.

To further aid in solving the processing problems, several mineralogical studies would be advisable. Etching tests to determine the solubility of the various manganese-bearing phases would aid in solving the problems involved in chemical separation methods. An indication of the dissolution properties of the various phases could rapidly be determined. Liberation studies would produce concrete grain-size figures along with quantifying the liberation information important in examining physical separation methods. Finally, a modal analysis would aid in both physical and chemical separation problems. By determining the mineralogy, the manganese content, and distribution of phases using Automated Image Analysis interfaced with a Microprobe, the distribution of manganese-bearing phases and the manganese in those phases can be quantified.

# APPENDIX A-1

# CORRESPONDENCE

Appendix A-1 DSS File No.: 07S!.23440-5-9216

## Work Statement

1. Title: Sampling and Analysis of New Brunswick Manganese Deposits

2. Purpose:

The contractor shall collect a number of samples from two sites in New Brunswick that have been identified as having large resources of manganese. The sites have been identified as the Plymouth area and the South Hartford area.

Following acquisition of the samples, qualitative mineralogy followed by detailed quantitative mineralogy and quantitative chemical analysis will be performed.

3. Work Plan:

a) Sampling

In consultation with the Scientific Authority and the Province of New Brunswick geologists, the two sites will be examined for the selection of 4 locations at each site. Trenching will be done to extract a 200 kg representative sample from each of the 8 locations. The trenches will be of a length and depth appropriate for representative sampling as agreed to by the geologists of the Province of New Brunswick. The samples will be identified, stored separately and reserved for metallurgical process testing. The deposit is covered by Mineral Claims Numbers 892, 893 and 894; arrangements shall be made between the contractor and the claim holder, "Maritime Resources Research Limited" to take samples from the deposit.

b) Analyses

b) Analyses

The trench samples will be analysed by quantitative mineralogical and chemical techniques, which will encompass the following:

Mineralogy

- identification of the mineral phases in the sample
- SEM and microprobe image analysis, to identify the phases which contain the elements of interest, with regard to process development
- other techniques suggested by the contractor that will assist in making process assessments based on mineralogy

Chemical analyses

- Quantitative chemical analyses will be performed on the samples based on the constituents identified by the mineralogy.
- Analytical techniques may include X-ray diffraction, atomic absorption, wet analysis, and other techniques available to the contractor that will increase the understanding of the samples.
- The oxidation state(s) of the manganese minerals is of particular significance.

4. General Contracting Conditions

Although the contract is written as a single document, the successful contractor may sub-contract a portion to a specific expert

in that particular field to best accomplish the objectives of the contract.

The total contract should be completed within 3 months following the signing of the contract, and preferably it shall be completed within 4 to 6 weeks of the signing of the contract.

## 5. Reporting

A short (e.g. 1 page) Progress Report shall be sent to the Scientific Authority at the end of the first month, reporting that month's activity. A draft Final Report shall be submitted to the Scientific Authority, for approval, at the end of the contract period. The Final Report (20 copies) shall be issued no later than one month following approval by the Scientific Authority of the draft Final Report.

**rpc**

research and productivity council
conseil de la recherche et de la productivité

November 13, 1985

Dr. W.J. Wilson
Atlantic Analytical Services
275 City Road
Saint John, N.B.
E2L 3N3

Dear Dr. Wilson:

I have enclosed a cost summary for the mineralogical studies necessary for the work outlined in the Work Statement of the DSS Request for Proposal No. 07SQ.23440-5-9216. I have given you an itemized cost for one bulk sample. This cost is calculated on the assumption that 8 bulk samples will be examined. If fewer than 8 bulk samples are studied then the quote will be revised.

I realize that the amount is in excess of the total contract; however this is the minimum amount of work required to make a process assessment as outlined in the work statement.

A detailed proposal is being prepared and will be sent to you on Friday.

Best regards,

John A.R. Stirling
Petrologist

JARS/gj
Encl.

MINERALOGY, GRAIN SIZE AND LIBERATION OF
NEW BRUNSWICK MANGANESE DEPOSITS

Eight, 200 kg Bulk Samples to be supplied by Atlantic Analytical.

Cost of Mineral Analyses for Each Bulk Sample

DRAFT

| Item | | | | |
|---|---|---|---|---|
| 1. | Coarse-crushing, Homogenization, splitting of bulk sample | | | |
| | 10 hrs | Lab Asst. 1 @ $20.00 | | $ 200.00 |
| 2. | Pulverizing to -100 mesh, sieve analyses +100, -100+48, -48+25, -25+10, -10 microns | | | |
| | 4 hrs | Lab Asst. 1 @ $20.00 | | 80.00 |
| 3. | Preparation of 6 polished grain mounts (Head and 5 size fractions) | | | |
| | 6 hrs | Lab Asst. 1 @ $20.00 | | 120.00 |
| 4. | Mineralogy, Grain Size and Qualitative Liberation of 6 polished samples | | | |
| | 42 (7 hrs/p.s.) | Prof. 1 @ $48.00 | | 2,016.00 |
| | 12 (2 hrs/p.s.) | Prof. 2 @ $64.00 | | 768.00 |
| | 24 (4 hrs/p.s.) | SEM/EDS Rental $35.00 | 840.00 | |
| 5. | Preparation of Rept. A. Data Interpretation<br>B. Comparison of Mineral and Chem. Analysis<br>C. Recommendations | | | |
| | 7.25 | Prof. 1 @ $48.00 | | 348.00 |
| | 7.25 | Prof. 2 @ $64.00 | | 464.00 |
| | | | Total Labour | $3,996.00 |
| | | | 8% Fee | 319.69 |
| | | | Expenses | 840.00 |
| | | | Total | $5,155.69 |
| 6. | Total for 8 Samples | | | $41,245.44 |

NOTE: The above costs have been determined on the assumption that the 8 bulk samples will be examined.

Total chemical analyses will be necessary on each sieve fraction in order to calculate proper mineral balances. The RPC lab could do whole rock analyses for the 48 samples at $8/25^{00}$ per sample.

## APPENDIX A-2

The following tables contain petrographic notes for samples P1, P2, P3, P4, NH1, NH2 and NH3. Each fragment type is described. Column 2 lists the minerals separated into transparent (a,b,c...) and opaque (1,2,3) phases. Brief notes on texture and size are given in the third column. Notice the expressions "K-spar" and "Na-spar" are frequently used. These are shortened forms of potassium feldspar and sodium feldspar (albite), respectively. The Ti oxide mineral often listed is either anatase or brookite. Finally, any mineral listed by the elements contained in it is too fine-grained to identify more than qualitatively. SEM/EDS techniques were used for this.

Sample P1

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 1 (31.5% of sample population) | (a) Na-spar (albite)<br>(b) FeK mica<br>(c) MnFe(K)MgAl silicate (chlorite)<br>(d) quartz<br>(e) Mn/Ca silicate<br>(f) rhodonite<br>(g) rhodochrosite<br><br>(1) psilomelane<br>(2) pyrolusite<br>(3) manganite<br>(4) manganoilmenite<br><br>(5) ilmenite<br>(6) CsZrSrBr<br>(7) hematite (Ti) | (a) (b) (c) (d) finely intergrown (1-5 micron level)<br>(f) (g) irregular blebs (30-200 micron) of mixture found in 1/10th of the fragments<br>(1) 1/5 of the fragments contain minor (<1%) subequant blebs (30-100 micron) - spongy, sometimes contain (e) Mn/Ca silicate<br>(3) 1/5 of the fragments (generally different fragments from those above) contain subequant manganite blebs (15-60 micron)<br>1/10 of fragments contain manganite with minor pyrolusite (2) veins (1-5 micron across)<br>(4) (5) (7) and sometimes (2) in all fragments as acicular to equant grains<br>- <1/2%-6% of fragment<br>- 1-50 micron long<br>- one fragment contains two large subequant grains of (4) 75-100 micron in size<br>(b) trace tiny (1-5 micron) grains<br>(d)/(c) large grains/"fans" found in trace amounts (75-100 micron) |
| Type 2 (7.8% of sample population) | (a) quartz<br>(b) Na-spar<br>(c) calcite<br>(d) Ca silicate<br>(e) Fe(Mn) chlorite<br>(f) white mica<br>(g) apatite<br><br>(1) Ti oxide<br>(2) pyrite | (c) cryptocrystalline to medium grained calcite, 45-60% of fragment<br>(b) (a) (d) (c) (f) minor amounts, fine-grained interstitial (e) sometimes as large (25-75 micron) "fans"<br>(g) very small (5-10 micron) rare apatite grains<br>(1) (2) rare irregular grains 5-15 micron in size<br>- brown "gel" evident usually |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| **Type 3 (10.0% of sample population)** | (a) calcite<br>(b) K-spar or Na-spar<br>(c) quartz<br>(d) Fe chlorite<br><br>(1) Fe oxide<br>(2) pyrite<br>(3) hematite | (a) from 65-95% of grain, fine to medium-grained<br>(b) (c) (d) finely intergrown (25-80 micron) with calcite (a)<br>(c) / (d) sometimes present as rare large (40-100 micron) grains/"fans"<br>(1) (2) fine equant anhedral grains (1-5 micron), only rarely observed<br>(3) in one fragment - traces of acicular hematite |
| **Type 3a (3.9% of sample population)** | (a) Mn(Ca) carbonate (rhodocrosite)<br>(b) quartz<br>(c) FeMn chlorite<br>(d) white mica<br>(e) rhodonite | (a) coarse-grained, one fragment is a single crystal<br>(b) fine to medium-grained mozaic mass beside carbonate and sometimes interstitial at (25-50 micron range)<br>(c) present generally as feathery masses or "fans"<br>(e) in one fragment very minor irregular grain ( 75 micron across) |
| **Type 4 (12.3% of sample population)** | (a) Mn(Ca) carbonate (rhodocrosite)<br>(b) Fe(Mn) chlorite<br>(c) Fe(Mn)K mica<br>(d) CaP (apatite)<br>(e) quartz<br>(f) K-spar<br><br>(1) hematite<br>(2) manganite<br>(3) psilomelane<br>(4) hausmannite<br>(5) pyrolusite<br>(6) magnetite | (a) predominant gangue mineral with (b) (c) (e) intergrown at 10-25 micron range (as much as 60% of gangue)<br>(d) small grains (5-10 micron) found in two fragments (trace)<br>(a) sometimes observed as large (25-60 micron) spongy equant blebs in massive hematite (1)<br>(1) anywhere from 10 to 70% of fragment<br>-acicular (or irregular) to massive<br>-often shows layering defined by varying concentrations of hematite (1)<br>(2) 3 fragments contain equant manganite blebs (10-50 micron) never more than 1% of fragment<br>-one fragment contains massive manganite (2) intergrown with massive hematite (1) - they appear to have remobilized (swirled texture of massive phases)<br>(3) one fragment contains small semi equant blebs (25-60 micron across) (<1%)<br>-one fragment contains large irregular blebs of psilomelane that have "flowed" around hematite (1) ( 25% of grain)<br>(4) one fragment contains very minor hematite (1) and a vein ( 25-50 micron across) of hausmannite and pyrolusite (5)<br>(6) one fragment contains traces of anhedral to subhedral manganite<br>- one fragment contains a portion of Type carbonate C |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 5 (3.9% of sample population) | (a) quartz<br>(b) K-spar<br>(c) Fe chlorite<br><br>(1) psilomelane<br>(2) pyrolusite<br>(3) bixbyite<br>(4) hematite<br>(5) hausmannite<br><br>(6) manganite | (a) (b) (c) 10-40% of fragments<br>-usually fine-medium-grained except where interstitial to psilomelane (pyrolusite then at 10-75 micron range)<br>(a) one fragment contains 2 large (50-100 micron thick) qtz veins<br>(1) (2) (5) finely intergrown (psilomelane dominant) at 10-50 micron range<br>-blocky<br>(3) acicular to massive "clump" present in one fragment<br>(4) acicular with gangue (parts of type 4) present in 2 fragments overprinting type 4 fragment?<br>(6) one fragment contains small semi equant manganite blebs also (50-100 micron)<br>(1) (4) (6) one fragment is only 60% ore minerals, present as large (100-250 micron across) blocky veins of psilomelane, with manganite blebs (50-75 micron) |
| Type 6 (3.9% of sample population) | (a) Na-spar<br>(b) MnKAl mica<br>(c) MnCaAlSi<br><br>(1) braunite<br>(2) pyrolusite<br>(3) manganite | (a) (b) sometimes (c) intergranular to Braunite (1)<br>(1) sperulitic to massive (although spongy)<br>-80-90% of fragment in most cases<br>-one fragment contains 45-50% spherulitic braunite with equant manganite blebs (10-50 micron across)<br>(2) 1/2 of fragments contain minor somewhat tabular pyrolusite inclusions in the Braunite (5-15 micron) |
| Type 8 (4.7% of sample population) | (a) quartz<br>(b) Na-spar<br>(c) Fe chlorite<br>(d) KFe mica<br>(e) Mn/Ca carbonate rhodochrosite | (a) (b) (c) (d) fine to medium-grained intergrown (a) (b) can be medium-grained sub round grains<br>(e) overgrown on above texture - 30-75% of grain |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 9 (3.9% of sample population) | (a) quartz<br>(b) K-spar<br>(c) Fe(Mn)AlMgSi (chlorite)<br>(d) calcite<br>(e) KFe mica<br>(f) KFeMg mica<br>(g) apatite<br><br>(1) manganoilmenite<br>(2) ilmenite<br>(3) pyrolusite<br>(4) hematite<br>(5) jacobsite<br>(6) Fe oxide | (a) (b) with (c) (e) or (d) (f) finely intergrown (5-15 micron level)<br>(g) tiny (1-5 micron) equant grains (trace only)<br>(1) (2) (3) and sometimes (4) 1-5% of grain<br>-large to fine acicular to tabular to irregular grains (1-75 micron across)<br>(5) rare, same as (1) (2) (3) and (4)<br>(6) two fragments contain semi equant manganite blebs (<1% of fragment) (25-50 micron across) |
| Type 10 (1.6% of sample population) | (a) quartz<br>(b) Na-spar<br>(c) white mica<br>(d) Fe chlorite<br><br>(1) Fe oxide | (a) (b) (c) (d) intergrown at (5-10 micron level)<br>-(a) (b) as lenses with (c) (d) around them<br>-(c) (d) are aligned<br>(1) trace small equant grains (1-10 micron across) |
| Type 11 (1.6% of sample population) | (a) Na-spar<br>(b) KFe mica<br>(c) quartz<br><br>(1) manganite<br>(2) jacobsite (Ti) | (a) (b) (c) finely intergrown at (1-10 micron range)<br>(1) (2) a "swarm" of thin (1-5 micron) veins, predominantly manganite (1) |
| Type 12 (1.6% of sample population) | (a) K-spar<br>(b) Fe chlorite<br>(c) Fe AlMg silicate<br>(d) Mn(Ca) carbonate rhodochrosite | (a) (b) (c) (d) finely intergrown (1-10 micron level)<br>-not a great deal of (d) rhodochrosite |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 13 (1.6% of sample population) | (a) K-spar<br>(b) quartz<br>(c) calcite<br>(d) Fe(Mn) chlorite<br>(e) KFe mica<br>(f) apatite | (a) (b) larger rounded grains (100-250 micron) with a matrix of (b) (c) (d) (e) finely intergrown (10-15 micron)<br>(f) minor small (5-10 micron) apatite grains |
| Type 14 (0.8% of sample population) | (a) quartz<br>(b) Mn chlorite (pennantite?) | (a) coarse clear quartz (only 2 crystals in the fragment)<br>(b) yellow/green plates and books ( 60-75 micron across) ( 10% of fragment) |
| Type 15 (0.8% of sample population) | (a) quartz<br>(b) rhodochrosite (minor Ca)<br>(c) chlorite<br><br>(1) CsZr oxide? | (a) mainly "annealed" quartz, medium grained with minor (b) and (c)<br>(c) is feathery medium-grained<br>(b) is fine-grained<br>(1) one equant grain (3 micron) present |
| Type 16 (0.8% of sample population) | (a) quartz<br>(b) K-spar<br>(c) FeK mica<br>(d) calcite<br>(e) apatite<br><br>(1) Fe oxide<br>(2) ilmenite | (a) (b) (c) (d) finely intergrown (5-15 micron)<br>(e) small equant grains (1-5 micron) rare<br>(1) (2) (d) (e) intergrown in a number of brown blebs some subhedral - altered? |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Carbonate C (3.1% of sample population) | (a) Mn(Ca) carbonate (rhodochrosite)<br>(b) quartz<br>(c) rhodonite<br>(d) Na-plag<br>(e) FeMn chlorite<br>(f) KMnFe(Mg) mica<br><br>(1) Fe oxide<br>(2) hematite<br>(3) manganite | (a) predominantly cryptocrystalline rhodochrosite (75-85%) with fine interstitial (b) (c) (d) (e) (f) (1-15 micron)<br>-rhodochrosite may be spherulitic<br>(1) trace equant grains (5-25 micron)<br>(2) type 4 (<30% acicular hematite) in layers or at edges in half the grains<br>(3) one fragment also contains a layer of spongy manganite (30-60 micron across) |
| Type AB (6.2% of sample population) | (a) quartz<br>(b) K(Fe) mica<br>(c) Fe chlorite<br>(d) FeK(Mn)Mg mica<br>(e) Na-spar<br>(f) calcite<br>(g) Ca silicate<br><br>(1) ilmenite<br>(2) hematite<br>(3) Fe oxide | (a) (b) (c) (d) (e) intergrown at (5-15 micron level)<br>-(b) (c) (d) often (50% of fragments) aligned with lenses of (a) (c) (fine mozaic texture)<br>(1) (3) (f) (g) dark "gel" (brown) pseudomorphs? found in three fragments<br>-(100-300 micron across)<br>-has shape of a calcite crystal<br>(1) (2) trace acicular (5-25 micron long) |

Sample P2

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 1 (17.8% of sample population) | (a) quartz<br>(b) Mn(K)Mg mica<br>(c) K(Fe,Mg) mica<br>(d) Ca phosphate<br>(e) Mn(K)AlSi<br>(f) Na(K) spar<br><br>(1) hematite (Ti)<br>(2) magnetite (Ti,Mn)<br>(3) ilmenite<br>(4) manganite<br>(5) psilomelane<br>(6) pyrolusite | (a) (b) (c) finely intergrown (5-15 micron)<br>(a) sometimes "mozaic" quartz veins (15-25 micron across)<br>(d) small grains (equant, anhedral) (5-10 micron)<br>(e) some fragments (4) contain 10-40% large blebs (2-15 micron) "overprinting" (a) (b) (c) (f) intergrowth<br>(1) hematite irregular grains (5-50 micron) (usually 5-10 micron)<br>(2) 1-3 micron grains, anhedral<br>(3) anhedral, 10-15 micron<br>(1) (2) (3) never more than 5% of fragment (in total)<br>(4) (5) may contain veins with both oxides (fine 1-5 micron) (3 fragments)<br>-one fragment contains thick (10-15 micron) vein<br>(4) (5) (6) 6 fragments contain minor (<1%) equant blebs (1-10 micron across) - generally only manganite (4), traces of (5) and (6) |
| Type 1a (24.3% of sample population) | (a) Na-spar<br>(b) KFe(Mg) mica<br>(c) quartz<br>(d) Fe-chlorite<br>(e) apatite<br><br>(1) CrMnFeZn oxide (spinel?)<br><br>(2) hematite (Ti)<br>(3) ilmenite<br>(4) Fe oxide<br>(5) manganite (Ca)<br>(6) pyrolusite<br>(7) psilomelane | (a) (b) intergrown at 2-10 micron level<br>(c) very minor<br>(c) (d) larger grains or "fans" (in the case of chlorite) (20-40 micron)<br>(e) minor (<10%) small equant grains<br>(1) (2) (3) (4) generally fine grains 2-5 micron although usually a few larger 5-15 micron<br>-generally irregular, elongate<br>-(1) very rare<br>-<1-10% in total of fragment<br>(5) -as fine (1-10 micron) veins in 1/2 of the fragments<br>-one fragment contains a large (10-25 micron) vein of (5) and (6) pyrolusite<br>-also as equant blebs (10-25 micron), as much as 1% of fragment, in 1/3 of the fragments<br>-rare (6) pyrolusite present<br>(7) one fragment contains 5% psilomelane blebs (similar to manganite blebs) |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| **Type 2 (10.3% of sample population)** | (a) calcite<br>(b) quartz<br>(c) chlorite | (a) fine to medium grained (one fragment in a single calcite crystal<br>(b) (c) 0-20% of fragment (one or both)<br>-interstitial to calcite (5-10 micron range)<br>(a) >80% of fragment |
| **Type 3 (3.2) of sample population)** | (a) calcite<br>(b) Na-spar<br>(c) Fe-chlorite<br>(d) K(Fe) mica<br>(e) quartz | (a) (b) (c) (d) (e) intergrown at 25-125 micron<br>-either (b) (c) or (b) (c) (d) with calcite (a) <80% |
| **Type 4 (13.0% of sample population)** | (a) quartz<br>(b) Na-spar<br>(c) Fe chlorite<br>(d) MnAl Silicate (minor K)<br>(e) MnMgAl Silicate<br>(f) K(Fe,Mn)Mg mica (<5%)<br><br>(1) BRAUNITE (sometimes minor Ca)<br>(2) MnBa (As,Rb) sulphate<br>(3) barite<br>(4) hematite<br>(5) manganite | (c) (d) (e) (f) combinations of these are intergrown with (a) (b) at 5 to 15 micron level<br>(1) irregularity outlined equant blebs (often spongy) (10-60 micron across) to massive 40-95% of fragment -often contains minor Ca<br>(4) 3 fragments contained traces of fine acicular hematite (<1/2% of fragments)<br>(2) (3) very fine equant grains (1-5 micron) only traces present<br>(5) 3 fragments contain blebs (5-30 micron) of manganite or fine veins (1-5 micron) -never major! |
| **Type 4a (1.1% of sample population)** | (a) quartz<br>(b) Na-spar (albite)<br>(c) MnMg chlorite<br>(d) Ba sulfate (barite)<br><br>(1) BRAUNITE (minor Ca) | (a) (b) (c) (d) finely intergrown at the 15-40 micron level<br>(1) -subhedral to anhedral (diamond shapes)<br>- 30-50 micron in size<br>- clumped in 3 layers |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 5 (6.2% of sample population) | (a) quartz<br>(b) KFe(Mg) mica (40%)<br><br>(1) Fe oxide<br>(2) Fe(Ti) oxide (hemalite) | (a) (b) finely intergrown (5-10 micron)<br>(1) (2) tiny grains (1-5 micron) equant<br>-~10-50% of fragment |
| Type 6 (2.2% of sample population) | (a) quartz<br>(b) Fe chlorite<br>(c) MnFe(Ca)Mg mica<br><br>(1) manganite<br>(2) Fe(Mn,Ti) oxide (magnetite)<br>(3) ilmenite | (a) (b) (c) finely intergrown (5-25 micron)<br>(a) 80% of fragment<br>(b) (c) 15%<br>(1) vein 20-30 micron across<br>(2) (3) fine irregular grains (1-5 micron)<br>(1) (2) (3) (4) 5% of fragment |
| Type 7 (5.4% of sample population) | (a) quartz | (a) medium to coarse grained<br>-often with many tiny inclusions<br>-many fluid inclusions<br>-3 fragments are single crystals |
| Type 8 (3.2% of sample population) | (a) quartz<br>(b) Fe chlorite<br>(c) K(Fe,Mg) mica<br>(d) calcite<br>(e) FeCa(Al)Si<br>(f) FeKMg mica<br><br>(1) Fe oxide<br>(2) pyrite<br>(3) Ti oxide | (a) (b) (c) intergrown (5-15 micron level)<br>(a) (d) in known "gel" pseudomorphs - 2.5/fragment<br>-perhaps altering calcite crystals? (100-200 micron across)<br>(f) surrounds pseudomorphs<br>(1) (2) (3) <1% of fragment<br>-small anhedral to subhedral grains<br>-(1-20 micron) |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 9 (3.7% of sample population | (a) Mn (Ca) carbonate<br>(b) Fe-chlorite<br>(c) K-spar<br>(d) quartz<br>(e) calcite<br><br>(1) hematite<br>(2) braunite<br>(3) manganite<br>(4) pyrolusite | (a) (b) (c) (d) finely intergrown at (5-10 micron range)<br>(e) one fragment contains a portion (on one end) of medium-grained (e) and quartz (d)<br>(1) acicular to massive (matted) (5-10 micron long)<br>(2) fine (15-30 micron) irregular intergranular with (1) hematite (in one fragment)<br>(3) (4) in one fragment small (15-40 micron) irregular blebs - contain acicular hematite inclusions |
| Type 10 (1.1% of sample population) | (a) quartz<br>(b) Fe chlorite<br>(c) K(Fe,Mg) mica<br><br>(1) ilmenite<br>(2) Fe oxide | (a) (c) intergrown at 5-15 micron<br>(b) mat-"feathery" chlorite - medium-grained<br>(1) (2) small irregular grains 2-5 micron in size (1/2-1%) |
| Type 11 (1.4% of sample population) | (a) quartz<br>(b) Na-spar<br><br>(1) manganite (minor Ca)<br>(2) pyrolusite | (a) (b) fine to med-grained 80% of fragment<br>-predominantly N-spar<br>-quartz often associated with Mn-oxides<br>(1) (2) finely intergrown (5-20 micron)<br>-spongy irregular vein/bleb 25-75 micron |
| Type 12 (5.4% of sample population) | (a) calcite<br>(b) Na-spar<br>(c) KFe(Mg) mica<br>(d) Fe chlorite<br>(e) quartz<br>(f) apatite | (a) 10-75 micron irregular blebs<br>(b) (c) (d) (e) finely intergrown known calcite at 2-10 micron level<br>(d) only about 1-3% of fragment<br>(f) trace, grains 10-15 micron in size, equant, anhedral |
| Type 13 (1.1% of sample population) | (a) Mn(Ca) carbonate (rhodocrosite)<br>(b) quartz | (a) massive to coarsely intergrown with (b) quartz at 50-150 micron level<br>(a) 85% of fragment<br>(b) 15% of fragment |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 14 (1.1% of sample population) | (a) KFe(Mg) mica<br>(b) Fe chorite<br>(c) K-spar<br>(d) calcite<br><br>(1) Fe oxide | (a) (b) (c) intergrown at 2-5 micron level<br>(d) (1) known "gel" blebs of intergrown calcite and Fe-oxide<br>-blebs 2-7 micron across |
| Type 15 (3.2% of sample population) | (a) quartz<br>(b) Mn chlorite<br>(sometimes minor Ca)<br>(c) Na-spar<br><br>(1) BRAUNITE (Fe,Ca)<br>(2) hematite<br>(3) psilomelane<br>(4) pyrolusite | (a) (b) (c) intergrown at 5-15 micron level<br>(1) equant, irregular blebs (15-40 micron across)<br>-spongy and sometimes containing hematite inclusions<br>-5-10% of fragment<br>(2) acicular to anhedral (1-6 micron) - throughout fragment but concentrated in bands<br>-5-15% of fragment<br>(3) (4) finely intergrown (1-5 micron) as veins<br>(20-40 micron across) and large irregular blebs<br>(100-300 micron) 2-15% of fragment |

Sample P3

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 1 (20.9% of sample population) | (a) quartz<br>(b) FeK mica<br>(c) Na-spar<br>(d) chlorite<br>(e) MnCa carbonate (rhodochrosite)<br><br>(1) hematite<br>(2) ilmenite<br>(3) Ti oxide<br>(4) manganite<br>(5) psilomelane | (a) (b) (c) finely intergrown (1-10 micron)<br>(a) some larger sub equant (40-60 micron) grains in 2 fragments<br>(d) med-grained "plates" or "fans" in 4 fragments<br>(e) trace of large irregular spongy blebs (30-75 micron across) sometimes<br>(1) (2) (3) irregular to acicular grains (3-15 micron across) 1-3% of fragment<br>(4) 1/4 of the fragments contain small (1-5 micron) manganite veins (<1/2% fragment)<br>(5) one fragment also contains minor psilomelane in the (manganite (4) veins |
| Type 2 (31.9% of sample population) | (a) Na-spar<br>(b) quartz<br>(c) Fe(Mn) chlorite<br>(d) FeK(Mg) mica<br>(e) MnAl silicate<br>(f) MnCa carbonate (rhodochrosite)<br><br>(1) manganoilmenite<br>(2) ilmenite<br>(3) pyrophanite<br><br>(4) hematite<br>(5) magnetite<br>(6) manganite<br>(7) psilomelane<br>(8) pyrolusite | (a) (b) (c) (d) finely intergrown (1-10 micron)<br>(a) (b) / (c) up to 5% large (25-75 micron) sub equant grains/"fans" in 20% of the fragments<br>(f) 1-2% of fragments large (25-100 micron) spongy equant grains in 10% of grains<br>(b) one fragment contains a medium-grained lense/vein at one end<br>(e) trace small (<10-30 micron) equant grains<br>(1) (2) (3) (4) acicular to irregular grains (5-25 micron long) <1% to 5% of fragment<br>(6) 1/3 of fragments contain fine (1-5 micron) manganite veins (from only 1 to a dozen per fragment)<br>-1/5% of fragments contain trace to 1% irregular to equant manganite blebs, 2 fragments contain intergrown pyrolusite (8) - (5-25 micron across)<br>(7) 1/10 of the fragments contain larger (5-40 micron across) equant to sub equant blebs<br>(5) one fragment contains trace subhedral magnetite grains (25-30 micron) |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 3 (1.4% of sample population) | (a) quartz<br>(b) KFeMg mica<br>(c) CaFe mica<br>(d) Na/Ca spar<br>(e) Fe chlorite<br>(f) CaFeMg<br><br>(1) Fe oxide (minor) | (d) (a) minor (f) medium-grained (100-750 micron level)<br>(d) is somewhat altered to (c) (b)<br>(e) fine feathery masses (100-250 micron across)<br>(1) minor Fe oxide |
| Type 4 (11.4% of sample population) | (a) quartz<br>(b) MnAl silicate (minor Ca or K)<br>(c) KFeMg mica<br>(d) Na-spar<br>(e) apatite<br>(f) MnCa carbonate<br>(g) Fe-chlorite<br><br>(1) hematite<br>(2) manganite<br>(3) braunite<br>(4) magnetite<br>(5) jacobsite | (a) (b) (c) (d) sometimes (f) intergrown at 5-15 micron range<br>(a)/(g) sometimes present as large (40-60 micron) grains/"fans" 1% of fragment<br>(e) trace small equant grains (10-25 micron across)<br>(1) irregular to acicular to massive (matted) hematite -20-30% of fragment<br>(2) 3 fragments contain manganite lenses (infiltrating) or small equant blebs (50-70 micron) (1-15% of fragment)<br>(3) (5) one fragment contains small (15-75 micron) irregular to equant blebs (<1% of fragment)<br>(4) 3 fragments contain minor (<1%) euhedral magnetite (30-75 micron across) |
| Type 5 (5.0% of sample population) | (a) quartz<br>(b) Na-spar<br>(c) calcite<br>(d) apatite<br>(e) chlorite<br><br>(1) Fe oxide<br>(2) psilomelane<br>(3) manganite | (a) or (b) medium to coarse-grained, often yellow/brown stains<br>(a) sometimes mozaic texture<br>-one fragment is a single grain<br>(c) one fragment contains medium-grained calcite with (a) quartz<br>(d) one fragment contains a large (5 micron) euhedral apatite crystal<br>(1) small equant grains (5-10 micron) or veins between gangue<br>(2) (3) one fragment contains a mass of intergrown (2) and (3) on one edge |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 6 (4.0% of sample population) | (1) hausmanite<br>(2) psilomelane<br>(3) pyrolusite<br>(4) manganite<br>(5) bixbyite<br>(6) jacobsite<br><br>(a) Na-spar<br>(b) MnCaAl silicate<br>(c) quartz | (A) finely intergrown masses (10-50 micron range)<br>minor pyrolusite, manganite, psilomelane<br>(B) one fragment is massive hausmanite with psilomelane and<br>pyrolusite (minor) along cracks<br>(C) blebs (10-100 micron)<br>-manganite or psilomelane and pyrolusite intergrown<br>(D) fine veins (1-10 micron) of psilomelane<br>-one fragment contains a jacobsite vein<br>(1) (2) (3) (4) various combinations (40-90% of fragment)<br>(a) (b) or (c) gangue minerals<br>(a) (b) finely intergrown (5-15 micron level)<br>(c) medium-grained and often stained yellow/brown |
| Type 7 (0.7% of sample population) | (a) calcite<br>(b) quartz<br>(c) Fe chlorite<br>(d) white mica<br>(e) Na-spar<br><br>(1) Fe oxide | (c) (d) predominant phases finely intergrown (2-10 micron range)<br>(a) a few large (10-50 micron across)<br>(b) (e) equant grains (10-50 micron across)<br>(1) trace of small (1-30 micron) equant grains (red "gel") |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 10 (10.7% of sample population) | (a) Na-spar<br>(b) quartz<br>(c) Fe(Mn,K) chlorite<br><br>(d) K(Fe) mica<br>(e) apatite<br>(f) calcite<br><br>(1) Fe oxide<br>(2) manganite<br>(3) psilomelane<br>(4) pyrolusite<br>(5) Ti oxide<br>(6) ilmenite<br>(7) manganoilmenite<br>(8) pyrite | (c) (d) 20-75% of fragment, finely intergrown (5-20 micron range) (d) more abundant, (c) often present as large (50-100 micron) "fans"<br>(b) sometimes as much as 40% fine (5-15 micron) mozaic quartz, often present as large (50-100 micron) grains<br>(a) sometimes present as large (50-100 micron) grains, minor<br>(e) trace small (5-10 micron) equant grains<br>(f) minor calcite sometimes present<br>(1) (2) (3) (4) (5) (6) (8) 1-5% of fragment<br>(1) small grains, usually equant (1-10 micron)<br>(2) small (1-5 micron) veins in 3 fragments -blebs (5-25 micron) in 1 fragment<br>(2) (3) (4) one fragment contains a lense ("seeping" into fragment) of mixed (1-15 micron range) manganite, psilomelane,and minor pyrolusite<br>(5) (6) (7) acicular to irregular grains (5-25 micron long) scattered throughout fragments<br>(8) two fragments contain very minor amounts of euhedral pyrite (5-25 micron across) |
| Type [illegible] (2.8% of sample population) | (a) Mn(Ca) carbonate (rhodochrosite)<br>(b) quartz<br>(c) Na-spar<br>(d) Fe chlorite<br><br>(1) Fe oxide<br>(2) pyrite | (a) predominantly rhodochrosite, fine-grained (15-25 micron range)<br>(b) (c) (d) minor interstitial (1-5% of fragment) in most fragments<br>(1) trace large (25-60 micron) equant to euhedral grains<br>(2) 3/4 of fragments contain euhedral to subhedral pyrite crystals (25-60 micron across) |
| Type 13 (1.4% of sample population) | (a) quartz<br>(b) chlorite<br>(c) calcite | (a) (b) very finely intergrown (5-10 micron range) with overprint of 30-50% brown "gel"<br>(c) one end is a medium-grained calcite lense?/vein? (only a portion remains) |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 14 (1.7% of sample population) | (a) Na-spar<br>(b) Ca phosphate<br>(c) apatite (Mn)<br>(d) Mn(Ca) carbonate<br><br>(1) Fe oxide (hematite)<br>(2) psilomelane | (a) (b) (c) (d) finely (10-30 micron) intergrown<br>(d) minor constituent near massive manganese oxides (when present)<br>(1) (2) small (1-15 micron) irregular grains<br>-intergrown with gangue<br>-(2) psilomelane is a minor component |
| Type 15 (0.7% of sample population) | (a) quartz<br>(b) Na-spar<br>(c) KFeMg mica<br><br>(1) magnetite<br>(2) hematite<br>(3) jacobsite | (a) (b) (c) very finely intergrown (1-10 micron), stained<br>- 45-55% of fragment<br>(1) subhedral (40-100 micron)<br>(2) acicular hematite - larger than in type 4 (30-50 micron long)<br>(3) small irregular blebs (10-40 micron) (<1/2% of fragment) |
| Type 16 (0.7% of sample population) | (a) Mn(Ca) carbonate<br>(b) quartz<br>(c) Na-spar<br>(d) Fe(Mn)KMg mica<br><br>(1) hematite (Mn, Ti)<br>(2) Fe oxide (hematite) | (a) large (150-250 micron across) equant spongy grains<br>-inclusions of quartz (b), Na-spar (c) and (1)<br>- 30% of fragment<br>(b) (c) (d) finely intergrown (10-30 micron)<br>(1) (2) tabular to acicular small (5-20 micron long) grains<br>- <1/2% of fragment |
| Type 17 (3.2% of sample population) | (a) Na-spar<br>(b) MnFeKMg mica<br>(c) quartz<br>(d) MnCaAl silicate<br><br>(1) manganoilmenite<br><br>(2) braunite<br>(3) hematite<br>(4) manganite | (a) (b) (c) (d) finely intergrown (5-20 micron range)<br>-(c) is very minor<br>-(d) small equant grains (5-20 micron)<br>(1) (2) (3) (4) 0-1/2% of fragment<br>(1) (3) irregular interstitial grains (10-30 micron)<br>-usually observed together<br>(2) rare irregular interstitial grains (10-15 micron)<br>(4) very rare irregular blebs |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 18 (1.4% of sample population) | (a) Fe chlorite<br>(b) sphene (minor Fe)<br>(c) KFe mica<br>(d) quartz<br>(e) CaFeAl silicate | (a) (c) medium-grained fibrous masses (mat)<br>-(c) 0-15% of fragment<br>(b) trace small (20-30 micron) granular crystals in chlorite<br>(d) (c) very minor (<1%) intergranular to (a) (c) |
| Type 19 (0.7% of sample population) | (a) quartz<br>(b) chlorite<br>(c) FeK mica<br><br>(1) manganite<br>(2) pyrolusite | (a) (b) (c) very fine intergrown (1-10 micron range)<br>(b) rare<br>(c) aligned<br>(a) minor large (30-75 micron) equant grains<br>(1) (2) fine (1-5 micron) veins - mixture of (1) and (2)<br>∿1% of fragment |
| Type 20 (0.7% of sample population) | (a) Fe chlorite<br>(b) quartz<br>(c) Na-spar<br>(d) AlFe(Mg)Si phosphate?<br><br>(1) manganite (Ca)<br>(2) Fe oxide<br>(3) Ti oxide | (a) (b) (c) finely intergrown (5-20 micron) somewhat lineated<br>(d) fine grains (2-5 micron) sub equant<br>(1) small (50-100 micron wide) lense (?) at edge of fragment<br>(2) (3) minor irregular grains (1-15 micron long |
| Type 22 (0.7% of sample population) | (a) calcite | (a) medium-grained calcite (100-300 micron) |

Sample P4

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 1 (12.7% of sample population) | (a) quartz<br>(b) MnFeKMg mica<br>(c) FeMn chlorite<br>(d) MnCa carbonate<br>(e) MnCa silicate (trace)<br><br>(1) FeTi oxide (ilmenite)<br>(2) Ti oxide<br>(3) Fe oxide (hematite)<br>(4) MnO (manganite) | (a) (b) (c) finely intergrown (<10 microns)<br>(a) (c) can be fine-grained (10-50 microns) scattered throughout fragment<br>(d) (e) as larger equant (30-75 micron on average) spongy grain mixture (irregular outline) (0-3% of fragment)<br>(a) one fragment contains a quartz vein (15-30 micron across)<br>(1) generally anhedral acicular to subequant (usually ≤10 but rare larger grains (coatings on Ti oxide often) (30-50 micron)<br>(2) same as above, although usually somewhat acicular only (often as with (1))<br>(3) usually elongate irregular grains (5-15 micron), although sometimes as large as 25 micron - hematite<br>(4) contains fine (1-5 micron) veins and irregular sub equant blebs (7 fragments) (1-15 micron)<br>-usually <1% of fragment<br>-manganite or hausmanite probably<br>-very minor pyrolusite, psilomelane<br>(1) (2) (3) (4) 1/2-2% of fragment |
| Type 1a (4.9% of sample population) | (a) quartz<br>(b) KFe(Mg) mica<br>((c) other white micas<br><br>opaque (1) FeO<br>(2) Fe(Ti) oxide (hematite)<br>(3) manganoilmenite<br>(4) Ti oxide (sometimes)<br>(5) Mn oxide | (a) (b) finely intergrown (1-10 micron)<br>(1) (2) (3) (4) see Type 1<br>(5) very minor manganite blebs (5-15 micron across)<br>(1) (2) (3) (4) (4) usually less than in type 1 (<1/2-1%) |

Sample P4

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 1b (1.0% of sample population) | (a) quartz<br>(b) K/Na-spar<br>(c) KMgFeAlSi (minor Mn) (mica)<br>(d) FeAlK silicate<br><br>(1) Fe(Ti,Mn) oxide (magnetite)<br>(2) FeTi oxide (ilmenite)<br>(3) manganite | (a) (b) (c) (d) all intergrown (1-5 micron)<br>(a) large equant grains (10-40 micron)<br>(d) small round grains (10-40 micron)<br>(2) predominant (1-15 micron), often elongate<br>(1) very small grains (1-5 micron)<br>(3) minor manganite<br>(1) (2) (3) from 2-5% of fragment |
| Type 2 (6.9% of sample population) | (a) Fe-rich chlorite<br>(b) Fe/Mn carbonate (manganese-rich siderite)<br>(c) quartz<br>(d) Fe(Mn)Al silicate<br>(e) K-spar | (a) (b) (e) medium-grained carbonate and chlorite and K spar (25-100 micron or more sometimes)<br>(a) (c) large quartz blebs with feathery chlorite within (50-100 micron)<br>(d) minor dark Fe(Mn)Al silicate in carbonate grains |
| Type 3 (1.0% of sample population) | (a) quartz<br>(b) K (MgFe) mica<br>(c) MnKAl silicate<br><br>(1) MnFe oxide (jacobsite)<br>(2) Fe oxide<br>(3) FeMn oxide (bixybite) | (a) (b) medium-grained quartz (1) with mica (2)<br>(c) a vein of MnKAl silicate above edge (1-10 micron)<br>(1) large massive blebs of MnFe oxide - jacobsite (50-100 micron)<br>(2) (3) small grains bixbyite (2) and Fe oxide(s) (<1%) (5-25 micron) |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 4 (3.4% of sample population) | (a) FeKMg mica<br>(b) Na-spar<br>(c) quartz<br>(d) Fe chlorite<br>(e) K mica<br>brown bleb:<br>(w) bixbyite<br>(x) Na-spar<br>(y) FeMn silicate<br>(z) Fe(K)Al silicate<br><br>(1) Mn oxide (manganite)<br>(2) FeCeBrZrNd? | (a) (b) (c) (d) crypto to fine-grained mica (a), Spar (b), quartz (c), chlorite (d) (intergrown at 10-25 micron range)<br>brown blebs-"gel" blebs (granular) containing fine intergrowths of (w) (x) (y) (z)<br>(1) a thin vein of (1) (1-5 micron) surrounded by (e)<br>(2) trace (1-5 micron across) equant grains |
| Type 5 (21.4% of sample population | (a) quartz<br>(b) KFe(Mn) mica<br>(sometimes minor Ti)<br>(c) K-spar/Na-spar<br>(d) Mn(Ca) carbonate<br><br>(rhodochrosite)<br>(e) Fe-chlorite<br>(f) MnTiKAl silicate<br>(g) Mn(Fe,Al) silicate<br>(h) MnFe(Al,K) silicate<br>(i) apatite<br><br>(1) psilomelane<br>(2) hausmanite<br>(3) braunite<br>(4) jacobsite<br>(5) bixbyite<br>(6) pyrolusite<br>(7) manganite<br>(8) magnetite<br>(9) hematite | gangue: assemblages finely intergrown at (5-25 micron range)<br>A (g) (h)<br>B (a) (b) (c) sometimes with (f) or trace (i)<br>C (d) with (a) (c) or (e)<br>D (e) (mat chlorite) sometimes with medium-grained (a) quartz<br>(1) traces of small grains (1-20 micron across)<br>ore minerals: from 15-90% (on average, 50%) of fragment<br>A-predominant texture/assemblage<br>-(1) (2) (6) or (5) and minor (3)<br>-finely intergrown (1-10 micron level) masses usually massive, but sometimes with many fine inclusions of gangue material (spongy)<br>-(b) or (5) only a minor constituent<br>B-blebs-equant to sub equant with irregular outlines (generally 5-25 micron across)<br>-of (7) manganite, (1)/(6) core/rim, (3) braunite (minor if present)<br>C-veins, thin (1-10 micron across)<br>-(1) psilomelane, (7) manganite, (4) jacobsite or (5) bixbyite rare (2) hausmanite<br>D-euhedral to subhedral (8) magnetite (25-60 micron across) crystals sometimes with wormy inclusions of (1) psilomelane? (9) hematite?<br>-found in 3 fragments |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 6 (13.7% of sample population) | (a) Mn/Ca carbonate (rhodochrosite)<br>(b) MnCa silicate<br>(c) FeAl(Mn,K,Mg) silicate (mica)<br>(d) Fe silicate<br>(e) Fe/Ca phosphate<br>(f) MnFe chlorite<br>(g) quartz<br>(h) FeK(Mg) mica<br><br>(1) hematite<br>(2) magnetite (Mn)<br>(3) manganite<br>(4) pyrolusite<br>(5) psilomelane<br>(6) magnetite<br>(7) pyrite<br>(8) chalcopyrite | (a) (b) (c) (d) (e) (f) (g) (h) finely intergrown at 5-15 micron level<br>-assemblages of:<br>A (a) (b) (e) (g) (h)-minor phosphate (c), most common assemblage<br>B (c) (d) in a layer<br>C (e) (f) in a layer of less hematite (1) and some Fe(Mn) oxide (2)<br>(f) 2 fragments contain mat chlorite veins (10-25 micron wide)<br>(1) acicular to irregular elongate to massive (matted)<br>-all texture sometimes found in one fragment<br>-5-25% of fragment<br>-may show layering defined by concentration of hematite<br>(2) Fe(Mn) oxide - intergranular irregular grains in low density hematite layers, not present in all fragments<br>(3) 2 fragments contain (10-15%) manganite "seeping" into fragments<br>(4) (5) minor small equant blebs (10-20 micron) (in 3 fragments)<br>-3 fragments contain thin (1-5 micron) veins, too<br>(6) euhedral to subhedral (resorbed) grains (20-60 micron across) found in 2 fragments (1/2-1%)<br>(7) 2 fragments contain euhedral pyrite the same size range as magnetite (6)<br>-one fragment also contains trace (8) cpy. |
| Type 7 (1.0% of sample population) | (a) FeKAL(Mg) mica<br>(b) Fe/Mn chlorite (minor K)<br><br>(c) Na-spar<br>(d) FeMnMgAlSi (chlorite)<br><br>(1) zircon<br>(2) Fe oxide<br>(3) CeLaFeWYrZrAs?<br>(4) CoAsFeS (arsenopyrite/cobaltite?) | (a) (b) (c) (d) intergrown (freely) (1-10 micron level)<br>(d) coarser than (b) sometimes as "fans"<br>(1) (2) (3) (4) all very small grains (1-10 microns), irregular, or equant (in the case of (2)) |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 8 (13.7% of sample population) | (a) FeMgAl silicate (chlorite)<br>(b) Fe(MgAl) silicate<br>(c) Fe/Mn carbonate (minor Ca) (manganese-rich siderite)<br>(d) quartz<br>(e) calcite<br><br>(1) chalcopyrite<br>(2) pyrite<br>(3) jacobsite | (a) (b) (c) (d) intergrown at (1-15 micron level)<br>-(c) predominant (45-95%)<br>(e) one fragment contains a fine calcite vein (10-25 micron wide)<br>(d)/(a) may be present as larger grains/"fans" (50-100 micron)<br>(c) sometimes spherulitic<br>(1) trace only<br>(2) in several grains, framboidal or subhedral (15-50 micron across)<br>(3) in one fragment (<1/2%) irregular to acicular grains (10-25 micron) |
| Type 8a (3.9% of sample population) | (a) quartz<br>(b) MnFe carbonate (iron-rich rhodochrosite)<br>(c) FeK(Mg)AlSi (mica)<br>(d) Fe(Mn) chlorite<br>(e) apatite<br>(f) Mn(Ca) carbonate (rhodochrosite) | (a) (b) (c) (d) intergrown fine to medium-grained (10-50 micron range)<br>-(a)/(d) sometimes large grains/"fans" (50-100 micron)<br>(e) small grains (5-15 micron) only traces<br>(f) one fragment contains a large spongy equant bleb of rhodochrosite |
| Type 9 (3.9% of sample population) | (a) Mn(Ca) carbonate<br>(b) quartz<br>(c) FeMn chlorite<br><br>(1) FeO<br>(2) magnetite<br>(3) pyrite | (b) minor - scattered<br>(c) fine grained<br>(a) fine to medium grained<br>(a) (b) (c) intergrown, predominantly rhodochorsite (a)<br>(1) anhedral with cores of pyrite (10-25 micron)<br>(2) euhedral to subhedral, sometimes containing small inclusions of pyrite (same size as seen with hematite)<br>(3) sometimes subhedral large grains seen with hematite also<br>(1) (2) (3) found in layers dusted with brownish red "gel" material |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 10 (2.0% of sample population) | (a) FeMn chlorite<br>(b) quartz<br>(c) FeK(Mn)Mg mica<br><br>(1) hematite<br>(2) manganite<br>(3) psilomelane | (a) ∿90% of grain mat chlorite (cryptocrystalline)<br>(b) minor med. grained quartz (not always present)<br>(c) minor FeK(Mn)MgAlSi (mica) associated with (1) hematite only (not always present)<br>(2) (3) fine vein (<10 micron) in one fragment<br>(1) acicular hematite as in type 6 |
| Type 11 (2.7% of sample population) | (a) quartz<br>(b) FeK(Mn)Mg mica<br><br>(1) psilomelane<br>(2) pyrolusite<br>(3) manganite<br>(4) hausmannite<br>(5) hematite | (a) predominantly fine to medium-grained -sometimes stained<br>(1) (2) (3) (4) found in one fragment<br>(1) (2) sub equant blebs (10-25 micron across) of intergrown material<br>(3) sub equant blebs (10-25 micron) - somewhat spongy<br>(4) (3) fine (1-5 micron) veins<br>(b) (5) Type 6 portion found in one fragment |
| Type 12 (2.9% of sample population) | (a) quartz<br>(b) FeMn(Mg) mica<br>(c) Fe(Mn) chlorite | (a) predominantly (95%-100%) fine to coarse mozaic quartz<br>(b) very minor fine grained<br>(c) radiating in one fragment |
| Type 13 (1.0% of sample population) | (a) Na-spar<br>(b) K(FeMg) mica<br>(c) FeK(Ti)Mg mica<br>(d) K(Mn,Fe) mica<br>(e) FeMn(Na)AlSi<br><br>(1) Fe oxide<br>(2) bixbyite<br>(3) manganite (Ca) | (a) (b) fine to cryptocrystalling (a) as lenses, (b) aligned<br>(c) (d) in opaque blebs with (4) core and sometimes (3) rims -blebs (25-75 micron across) - intergrown<br>(e) with manganite (4) in veins (<10 micron)<br>(1) equant grains (25-60 micron across) |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 14 (1.0% of sample population) | (a) MnK(Fe,Mg) mica<br>(b) rhodonite<br>(c) KFe(Mn) mica<br>(d) MnFeKMg mica<br><br>(1) braunite<br>(2) ilmenite<br>(3) manganoilmenite<br>(4) ZrCeMnSi? | (a) (b) (c) (d) finely intergrown 5-25 micron range<br>(1) minor (<1/2%) 5-10 micron in size, subhedral<br>(2) minor 5-10 micron in size, acicular to tabular<br>(3) minor 5-10 micron in size, acicular to tabular<br>(4) trace 1-10 micron in size, small equant grains<br>(1) (2) (3) (4) scattered through gangue 1-2% in total |
| Type 15 (2.9% of sample population) | (a) Na-spar<br>(b) MnFe(K) chlorite<br>(c) Fe chlorite (minor K)<br>(d) MnAl silicate<br><br>(1) Fe oxide<br>(2) bixbyite<br>(3) Mn(Ca) oxide (manganite)<br>(4) Ti oxide<br>(5) pyrite | (a) (b) (c) (d) gangue at the 10-30 micron range<br>-finely intergrown<br>(1) (2) (4) fine grains scattered (1-10 micron) acicular to irregular<br>(3) subequant blebs (10-15 micron)<br>(5) one fragment contains a single euhedral pyrite grain:<br>approximately 30 micron across |

Sample NH1

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| **Type 1 (12.4% of sample population)** | (a) quartz<br>(b) Na/K Spar<br>(c) MnFeK(Mg) mica<br>(d) Fe(Mn) chlorite<br>(e) FeK(Mg) mica<br>(f) apatite<br><br>(1) pyrite<br>(2) pyrophonite | (a) (b) (c) (d) (e) intergrown at (2-10 micron)<br>-either (a) or (d) (e)<br>-(c) often large patches<br>(f) large grains (15 micron) irregular equant (trace)<br>(a) (d) sometimes larger grains or "fans" 100-200 micron<br>(a) framboidal and euhedral<br>-generally mostly framboids<br>-often 2 generations (a) somewhat elongate and altered to Fe oxide<br>(b) very round - not altered<br>10-60 micron across<br>-anywhere from 5 to 30% of fragment<br>(2) dark grey/brown acicular grains (<1%) (5-15 micron long) in 5% of fragments |
| **Type 2 (29.8% of sample population)** | (a) quartz<br>(b) K-spar<br>(c) Fe(Mn) chlorite<br>(Mn sometimes not present)<br>(d) FeK(Mg) mica<br>(sometimes minor Mn)<br>(e) FeKMg mica<br>(f) FeTi(Mn,K)MgAlSi(chlorite)<br>(Ti only minor sometimes)<br>(g) zircon<br><br>(1) Ti oxide<br>(2) pyrite<br>(3) magnetite<br>(4) pyrophanite<br>(5) psilomelane<br>(6) pyrolusite<br>(7) manganite | (a) (b) (c) or (f) (with minor Ti only) with one of (d) (e) or (f)<br>-finely intergrown at 1-5 micron level<br>(g) traces of small (<1-3 micron) equant grains of zircon<br>(a) (c) sometimes present as larger (15-45 micron) grains/"fans"<br>(1) generally present as small (5-15 micron across) irregular to equant grains (<1/2% of fragments)<br>(2) present in 1/4 of fragments as small anhedral to euhedral grains (5-25 micron across (always <1/2% of fragment)<br>(7) (5) (6) one fragment contains minor (<1/2%) manganite blebs (15-35 micron) and a vein (10-25 micron across) of pyrolusite and psilomelane<br>(3) (4) (5) one fragment contains a vein (40-60 micron across) with a magnetite core, MnTi oxide on the outside irregular "wispy" psilomelane<br>-elsewhere there is a series of fine (1-5 micron thick) veins of psilomelane and minor manganite |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 2a (10.2% of sample population) | (a) quartz<br>(b) K-spar<br>(c) Fe(MnTi)KMg mica<br>(d) Fe(Mn)K(Mg) mica<br>(e) KFe(Ti) mica<br>(f) Fe(Mn,K) chlorite<br><br>(1) Ti oxide<br>(2) Fe oxide<br>(3) zircon<br>(4) chalcopyrite<br>(5) TaLaCeNdSmGdZrAlSi<br>(6) dark grey Mn oxide (manganite)<br>(7) pyrite | (a) (b) (c) (d) or (a) (b) (e) (f) intergrown at 1-10 micron range<br>-opaques $\leq$1/2%-1%<br>-grain lineated fabric<br>(1) irregular to acicular grains 5-10 micron<br>(2) (4) associated, similar to above<br>(4) only trace<br>(3) trace, similar size<br>(5) irregular similar size to above<br>(6) small irregular blebs in one train (trace)<br>(7) trace in sample of grains - anhedral |
| Type 3 (5.8% of sample population) | (a) quartz<br>(b) Na-spar<br>(c) KFe(Mg) mica<br>(d) Fe chlorite<br>(e) apatite<br><br>(1) Ti oxide | (a) (b) larger equant grains 10-60 micron<br>-$\leq$1/2% opaques<br>(c) (d) finely intergrown 10-15 micron around (a) (b)<br>(e) trace subequant grains 15-25 micron<br>(1) trace irregular to acicular 10-15 micron<br><br>- brown "gel" $\sim$10-20% of each fragment |
| Type 4 (3.6% of sample population) | (a) quartz<br>(b) K-spar<br>(c) MnCaFe(KMg)AlP silicate<br>(d) FeMn(K)MgAlSi (chlorite)<br>(e) KFe(Mg) mica<br><br>(1) Fe oxide<br>(2) Ti oxide | (a) (b) (c) (d) finely intergrown 2-20 micron range<br>(1) (2) trace in some grains - fine 2-10 micron range<br>(1) one fragment contains a fine (5-15 micron wide) vein |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 5 (0.7% of sample population) | (a) quartz<br>(b) KFe(Ti,Mg) mica<br>(c) Fe chlorite<br>(d) apatite<br>(1) LaCsNbGdFeZrAlSi | (a) (b) (c) finely intergrown at 10-30 micron range, (a) usually largest equant grains<br>(c) minor large fans (50-70 micron), often clumped platey<br>(d) one grain 25 micron<br>(1) trace, equant, 2-5 micron |
| Type 6 (2.2% of sample population) | (a) quartz<br>(b) FeK(Mg) silicate<br>(c) FeMnMgAlSi (chlorite)<br>(1) acicular hematite<br>(2) Fe oxide | (a) larger equant blebs 15-25 micron<br>(b) (c) intergrown, intergranular to (a) quartz, 10-20 micron range<br>(1) acicular hematite (fine 5-20 micron)<br>(2) anhedral (similar size) |
| Type 7 (5.1% of sample population) | (a) quartz<br>(b) Na-spar<br>(c) FeMnMgAlSi (chlorite)<br>(d) FeMnK(Mg) mica<br>(1) pyrophanite<br>(2) Ti oxide | (a) (b) (c) (d) 1-10 micron range intergrown<br>(1) (2) small irregular grains (subhedral sometimes) (1/2-5 micron) <1/2% (usually trace amounts only) |
| Type 8 (8.0% of sample population) | (a) Mn(Ca) carbonate<br>(b) K(Fe) mica<br>(c) FeK(Mg) mica<br>(d) quartz<br>(e) apatite<br>(f) Fe(Mn) chlorite<br>(1) Ti oxide<br>(2) Fe oxide<br>(3) pyrite<br>(4) LaCeNdFeZrSiAl | (a) (b) (c) (d) finely intergrown 1-15 micron range<br>(d) may be equant grains (bit larger)<br>(a) 1%<br>(e) minor grains (subhedral) 5-25 micron, trace amounts only<br>(f) large "fans" 30-60 micron<br>(1) (2) (4) fine irregular to equant grains 2-8 micron<br>(3) framboidal (20 grains) in one fragment (20-50 micron) |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 9 (6.5 of sample population) | (a) quartz<br>(b) Fe(Mn) chlorite<br>(c) K(Fe,Mg) mica<br>(d) FeK(Mg) mica<br><br>(1) manganite<br>(2) psilomelane<br>(3) pyrolusite<br>(4) hausmanite(?)<br>(5) pyrite<br>(6) Ti oxide | (a) (b) (c) (d) finely intergrown combination of some or all of micas<br>(1) often many fine (1-5 micron) veins<br>-sometimes with minor (8) pyrolusite or (4) hausmanite<br>-blebs manganite sometimes also (2.20% of grain) (10-15 micron)<br>-with or without veins<br>-with or without psilomelane(2)<br>(1) (4) one frag. contains pseudomorphs after braunite layers of each (see SEM photo)<br>(5) one frag. contains 2 pyrite framboids (see type 1)<br>(6) minor an-subhedral (1-5 micron) Ti oxide grains may be present |
| Type 10 (1.4% of sample population) | (a) quartz<br>(b) FeMn chlorite<br><br>(1) Fe oxide<br>(2) FeMn oxide (jacobsite) | (a) coarse-medium grained<br>(b) (1) (2) intergrown in clumpy veins<br>-chlorite not always present |
| Type 11 (0.7% of sample population) | 3 layers<br>(a) FeMn chlorite<br>quartz<br>K-spar<br>white micas<br>minor Fe oxides<br>(b) FeMnMgAlSi(chlorite)<br>KFe(Mg) mica<br>(c) FeMn chlorite<br>KFe(Mg) mica<br>Fe oxide | (a) intergrown 10-25 micron<br>(b) intergrown 5-15 micron<br>(c) intergrown 5-15 micron<br>somewhat stained |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 12 (8.0% of sample population) | (a) K-spar<br>(b) FeK(Mn,Mg) mica<br>(c) minor Fe chlorite<br>(d) quartz<br><br>(1) pyrophanite<br>(2) Ti oxide (ilmenite)<br>(3) Fe oxide (hematite)<br>(4) Fe oxide<br>(5) manganite<br>(6) psilomelane<br>(7) pyrolusite<br>(8) jacobsite | (a) (b) sometimes (c) finely intergrown 2-5 micron range sometimes (d)<br>(1) (2) (3) -from <1/2 to 2% of fragment<br>-generally acicular to elongate irregular<br>- 2-10 micron at longest dimension<br>-usually all present though distribution varies<br>(4) very minute (<1-3 micron) grains (<1/2%)<br>(5) two fragment contains small (1-5 micron) veins and one fragment contains small (5-15 micron) equant blebs<br>(6) (7) (8) one fragment contains a large vein (35-60 micron wide) with a core of pyrolusite (7) then psilomelane (6) and on the outside jacobsite (8) |
| Type 13 (1.4% of sample population) | (a) Mn/Fe (minor Ca) carbonate<br>(b) K(Mg) mica<br>(c) FeMn chlorite<br>(d) MnFe(Ca,K)AlSi<br>(e) FeCa(Mg,Al,P)Si<br><br>(1) hematite | (a)-(c) finely intergrown 1-5 micron range<br>(d) equant grains (not mica)<br>(1) acicular to irregular to massive |
| Type 14 (0.7% of sample population) | (a) K/Na spar<br>(b) quartz<br>(c) FeKMgAlsi<br>(d) apatite<br><br>(1) MnTi oxide (Jacobsite or bixbyite)<br>(2) Fe oxide (hematite) | (a) (b) (c) finely intergrown 5-15 micron<br>-extinction of whole areas at one angle alligned slate<br>(1) (2) traces (1-6 micron) anhedral to subhedral |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 15 (0.7% of sample population) | (a) quartz<br>(b) Fe(Mn) chlorite<br>(c) white micas<br><br>(1) magnetite<br>(2) Fe oxide<br>(3) hematite<br>(4) pyrite | (a) (b) (c) finely intergrown (5-15 micron range)<br>(1) large euhedral grains (30-60 micron) ]<br>(2) smaller subequant grains (10-50 micron) ] 2-7% in total<br>(3) acicular grains (10-25 micron) ]<br>(4) cores of larger subequant (2) grains (rare) ] |
| Type 16 (0.7% of sample population) | (a) quartz<br>(b) apatite<br>(c) Mn silicate (tephroite)<br><br>(1) psilomelane<br>(2) MnFe oxide (bixbyite)<br>(3) pyrolusite | (a) (b) (c) fine tomedium-grained - approximately 15% gangue -mostly large irregular blebs (50-300 micron)<br>(1) (3) predominantly massive intergrown pyrolusite (3) and psilomelane (1) with (1) being more abundant (5-25 micron range)<br>(2) minor blocky masses of bixbyite (40-100 micron across) |
| Type 17 (0.7% of sample population) | (a) Na/K spar<br>(b) FeK(Mg) mica<br><br>(1) manganoilmenite<br>(2) Fe oxide (hematite)<br>(3) pyrophanite | (a) (b) finely intergrown 5-20 micron -<1% opaques<br>(1) subhedral 1-3 micron<br>(2) acicular 5-10 micron<br>(3) irregular 5-10 micron |
| Type 18 (0.7% of sample population) | (a) Fe chlorite | (a) mat chlorite fine to medium-grained feathery |

Sample NH2

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| **Type 1 (24.0% of sample population)** | (a) quartz<br>(b) FeMgAlSi (chlorite)<br>(c) K(Fe,Mg) mica<br>(d) Fe(Mn)MgAlSi (chlorite)<br>(e) KFe mica<br>(f) Fe(Mn)KMg mica<br><br>(1) Ti oxide<br>(2) LaCsNdSmZrSiAl?<br>(3) Fe oxide<br>(4) pyrite<br>(5) manganite<br>(6) psilomelane | (a) generally fine-grained (10-40 micron) mozaic texture<br>-50-80% of fragment<br>-locally minor large grains (40-80 micron)<br>-one frag. mozaic qtz vein<br>(b) (c) or (d) (e) finely intergrown with (a) qtz (10-20 micron)<br>(e) (f) or (f) large "fans" found locally of pure (f) or alternating (intergrown) (e) and (f)<br>-never more than 5% of fragment<br>(1) <1/2-1% fine (3-5 micron) irregular to subhedral grains<br>(2) trace fine (3-5 micron) irregular grains<br>(3) found in several grains as alteration of pyrite framboids (see Type 1 - NH1)<br>(4) very minor small (1-3 micron) equant grains found in couple of frags.<br>(5) in one fragment (5%) irregular, spongy blebs (25-50 micron)<br>(6) found in one fragment - blebs <10 micron across<br>- vein 60 micron thick |
| **Type 2 (1.6% of sample population)** | (a) Fe(Mn) rich chlorite<br>(b) Na-spar<br>(c) Fe-chlorite<br>(d) K(Fe)AlSi<br><br>(1) MnFe oxide (Jacobsite)<br>(2) MnFe(Ti) oxide (bixbyite)<br>(3) Mn oxide (psilomelane) | (a) medium-grained-feathery mat. chlorite with minor (1) irregular skeletal blebs (10-25 micron)<br>(b) (c) (d) other section-finely intergrown 10-15 micron range with very minor (2) small irregular blebs (5-10 micron)<br>(1) jacobsite, fine "intergranular" in chlorite "interlayered"<br>(2) (3) psilomelane and bixbyite blebs 20-30 micron and vein 40 micron thick |
| **Type 3 (1.6% of sample population)** | (a) quartz<br>(b) Mn(Fe) chlorite | (a) single quartz grain sometimes with minor small (60-100 micron) plates of (b) - vermicular chlorite? |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 4 (33.4% of sample population) | (a) quartz<br>(b) Fe-chlorite (Mn)<br>(c) KFe(Mg) mica<br>(d) Na-spar (albite)<br>(e) Ca(Mn) carbonate (calcite)<br>(f) Fe(Mn)KMg mica<br><br>(1) Ti oxide<br>(2) FeTi oxide (ilmenite)<br>(3) manganite<br>(4) psilomelane<br>(5) pyrolusite<br>(6) jacobsite<br>(7) pyrite<br>(8) Fe oxide | (a) from 10 to 60% silicified (fine mozaic quartz?)<br>(a) (b) (c) (d) finely and more coarsely aligned micas with elongate qtz (a) and albite (d) lenses -(1-5 micron range) or (5-10 micron range) intergrown<br>(e) fragment contains 1-5% finely intergrown (1-5 micron range) calcite<br>(f) one fragment contains 2 large irregular veins of (f) and psilomelane<br>(a) (b) some fragments contain minor large grains/"fans" (20-40 micron)<br>(1) (2) most of the fragments contain fine (1-10 micron) irregular, elongate ilmenite(2) and Ti oxide grains<br>(3) (4) about 1/4 of fragments contain either equant blebs<br>(3) manganite (40-60 micron)<br>(4) psilomelane (<10 micron) - more common<br>or fine veins (<10 micron)<br>-one or both manganite and psilomelane<br>(3) (5) (6) one fragment contains<br>(A) a large vein manganite and pyrolusite (5)<br>(B) fine veins of manganite (3) (with (f))<br>(C) blebs of manganite (3)<br>(D) larger blebs of jacobsite (6)<br>(7) (8) one fragment contains minor pyrite with Fe oxide (8) coatings |
| Type 5 (1.6% of sample population) | (a) Na-spar<br>(b) Fe(K)Mg mica<br>(c) K(Fe,Ca) mica<br><br>(1) Ti(Fe) oxide?<br>(2) Ti(MnFe) oxide (magnetite)<br>(3) Ti oxide<br>(4) manganite<br>(5) jacobsite | (a) (b) (c) intergrown at 5-15 micron scale<br>(1) (2) (3) minor (3-5 micron) anhedral to subhedral<br>(4) (5) intergrown (3-10 micron) in spongy blebs with (c) K(Ca)AlSi present locally (5-10%) |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 6 (3.9% of sample population) | (a) MnK mica<br>(b) Mn(Ca) carbonate<br>(c) MnFe(K) mica<br><br>(1) manganite<br>(2) psilomelane<br>(3) pyrolusite<br>(4) hematite | (a) (b) or just (c) finely intergrown at 2-5 micron level in irregular blebs (10-500 micron across)<br>-as much as 15% of fragment from 3%)<br>(2) predominantly psilomelane sometimes with finely intergrown (2-10 micron level) pyrolusite (3) and in one case acicular hematite (4)<br>(1) most fragments contain manganite either as fine (2-10 micron) intergrowths or large (200-500 micron) irregular masses<br>(3) two fragments contain small (5-15 micron) veins of pyrolusite |
| Type 7 (10.7% of sample population) | (a) calcite (minor Mn)<br>(b) quartz<br>(c) Na-spar (minor K sometimes)<br>(d) Fe chlorite<br>(e) K(FeMg) mica<br><br>(1) pyrite<br>(2) psilomelane<br>(3) Ti oxide<br>(4) Fe oxide | (a) 20-80% (usually 10%) of frag. large blebs 25-125 micron intergrown with:<br>(b) (c) and minor (d) or (e) (<1-10%)<br>(1) may contain -framboidal (see type 1-NH2)<br>-subhedral (same size or smaller than) 1% in one fragment<br>(2) one fragment - minor blebs psilomelane (<<1/2%)<br>(3) may contain trace irregular (2-5 micron)<br>(4) -as coatings on (1) framb.<br>-small grains (2-7 micron) in one fragment |
| Type 8 (10.2% of sample population) | (a) quartz<br>(b) Na-spar<br>(c) FeMn chlorite (Mn sometimes only minor)<br>(d) MnFe(Ti,K,Mg) mica<br>(e) Fe(Ca,K) mica<br>(f) Mn(K,Ca)AlSi<br>(g) MnCa silicate | Intergrown gangue<br>(c) (d) minor (a)<br>(a) (c) only minor Fe(Mn) chlorite (c)<br>(a) (b) (e) with Fe oxide - 1 to 5 micron range (intergrown)<br>(a) (h) (g) 1 to 5 micron range (intergrown)<br>(a) (i) 5 to 10 micron range (intergrown)<br>(a) (j) (i) Finely intergrown<br>Ore minerals: |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 8 (cont'd) | (h) Mn(Fe)Ca(P,Al)Si<br>(i) Fe(Mn)K(Mg) mica<br>(j) KFe(Mg) mica<br><br>(1) manganite<br>(2) psilomelane<br>(3) pyrolusite<br>(4) hematite<br>(5) bixbyite<br>(6) jacobsite<br>(7) magnetite | (A) predominantly irregular to equant blebs (10-70 micron) of:<br>(1)<br>(2) (3) pyrolusite rims or intergrowths (1-5 micron) and sometimes minor (4) hematite<br>(2) (5) (4) intergrown (1-5 micron) (5) and (4) are minor<br>(4) (2) with minor psilomelane<br>-these bleb types may all be present or some combination<br>-manganite (1) in two cases is present by itself<br>-from 15-35% of fragment<br>(B) - more intergranular (with gangue) blebly veins and masses (3 fragments in quartz)<br>Mixtures of:<br>(1) (6) (5) and very minor (7) intergrown at 2-10 micron range<br>(1) (6) (2) very minor (7) intergrown at 2-10 micron range with large veins of psilomelane (2) minor pyrolusite (3) (15-30 micron across)<br>-from 30-60% of fragment<br>(C) - large veins of psilomelane and minor pyrolusite (15-100 micron across)<br>-tend to be blocky<br>-one fragment contains veins of manganite (1) and jacobsite (6) and Mn(KCa) Al silicate (f) on the outside<br>(D) - one fragment contains blebs, large veins and acicular to anhedral fine (2-5 micron) hematite in a layer |
| Type 9 (3.0% of sample population) | (a) quartz<br>(b) Na-spar<br>(c) KFeMg mica<br>(d) Fe(K)Mg mica<br><br>(1) Ti oxide<br>(2) Fe oxide<br>(3) psilomelane<br>(4) pyrolusite | (a) (b) large grains (100-400 micron) subequant<br>(a) (c) (d) finely intergrown (5-15 micron) around large grains<br>(a) here as mozaic texture<br>(1) small sub-anhedral grains 2-5 micron<br>(2) often euhedral (cubic?) rgel grains (5-70 micron)<br>(3) (4) more fragment blebs (20-50 micron) intergrown psilomelane and pyrolusite |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 10 (3.0% of sample population) | (a) Fe(Mn) chlorite<br>(b) FeMgAl silicate (Mn)<br>(c) apatite<br>(d) FeK(Mg) mica<br><br>(1) hematite<br>(2) manganite<br>(3) psilomelane | (a) (b) intergrown with (1) hematite (5-10 micron)<br>(c) (d) finely intergrown fat (2-5 micron)<br>(1) fine (2-30 micron) irregular grains or blebs<br>-very minor acicular<br>-20-50% of fragments<br>(2) (3) irregular intrusive blebs (200-400 micron in length) of finely intergrown (5-10 micron) manganite and psilomelane or just manganite |
| Type 11 (1.6% of sample population) | (a) calcite (minor Mn)<br>(b) quartz<br>(c) Na(K)-spar | (a) 65-75% of fragment<br>(a) (b) (c) intergrown at (100-300 micron range) |
| Type 12 (0.8% of sample population) | (a) CaTiAl silicate<br>(b) Fe chlorite<br>(c) Na-spar<br>(d) K(Mg) mica<br>(e) CaFeMgAlSi (garnet?) | (a) (b) 5% of fragment<br>(c) (d) (e) more abundant<br>all intergrown at the 50-300 micron range |
| Type 13 (3.0% of sample population) | (a) quartz<br>(b) Na-spar<br>(c) K(Mn,Fe)Mg mica<br>(d) FeKMgAlSi<br><br>(1) pyrophanite<br>(2) ilmenite<br>(3) hematite<br>(4) LaCsNdSmZrSiAl? | (a) (b) (c) (d) (2-5 micron) finely intergrown<br>(1) (2) anhedral to subhedral grains (1-12 micron)<br>-mostly (1-3 micron)<br>(3) fine acicular grains (1-5 micron)<br>(4) trace (approx. 5 micron across) equant grain |
| Type 14 (0.8% of sample population) | (a) quartz<br>(b) Fe chlorite | (a) coarsely smeared silica with (b) chlorite between long feathery grains |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 16 (0.8% of sample population) | (a) quartz<br>(b) K(Fe)(Mg) mica<br>(c) MnFe(K)MgAlSi (chlorite)<br><br>(1) Ti oxide | (a)(b)(c) finely intergrown (5-15 micron)<br>(c) quite platey (only 2-5% of fragment)<br>(1) (5-10 micron) subhedral trains |

Sample NH3

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 1 (11.4% of sample population) | (a) quartz<br>(b) Fe(Mn) chlorite<br>(c) KFeMg mica<br>(d) FeKMg mica<br>(e) Na-spar (albite)<br>(f) Ca Phosphate (apatite)<br><br>(1) FeTi oxide (ilmenite)<br>(2) FeO<br>(3) Zircon<br>(4) TiO<br>(5) Mn(Ca) oxide (manganite) | (a) (e) large sub rounded grains (50-200 micron)<br>(a) -one grain contains "smeared" silica<br>-most grains contain cryptocrystalline mozaic silica<br>(b) (c) (d) all or any combination (chlorite usually present at 1-5%)<br>(b) a couple of fragments contain larger (50-100 micron) "fans"<br>(f) equant grains 1-2 micron across - only traces found<br>(a) (b) (c) (d) finely intergrown at (5-25 micron range)<br>(2) rgel FeO grains - euhedral - anhedral with pyrite cores (altered framboids) (5-100 micron)<br>(1) (3) (4) (5) fine irregular grains (1-10 micron)<br>(5) in one fragment <<1% blebby |
| Type 2 (2.6% of sample population) | (a) quartz<br>(b) K-spar (smeared)<br>(c) Fe(Mn) chlorite (1-2%)<br><br>(1) zircon<br>(2) FeO<br>(3) TiO | (a) (b) (c) intergrown at the 25-50 micron level<br>(1) (2) (3) fine (10-15 micron) irregular grains, <u>traces</u> to 1% |
| Type 3 (3.5% of sample population) | (a) quartz<br>(b) KFe(Mg)AlSi<br>(c) (Fe,Ti,K)Mg mica<br>(d) Fe chlorite<br><br>(1) Fe oxide (rgel)<br>(2) Ti oxide<br>(3) manganite<br>(4) psilomelane | (a) (b) (c) the micas "coat" the silica grains (in equant) at 1-35 micron range<br>(d) minor large "fans" 25-50 micron range<br>(1) found in all 1-10 micron in size<br>(2) trace 1-20 micron (irregular grains)<br>(3) in one fragment as a fine vein (<5 micron across)<br>(4) traces of blebs (10-20 micron across) in one fragment |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 4 (1.8% of sample population) | (a) quartz<br>(b) K(Fe) mica<br>(c) Fe chlorite<br>(d) MnFeMgAlSi (chlorite)<br>(e) Na-spar<br><br>(1) Fe oxide<br>(2) Ti oxide | (a) (b) couple of large (100-200 micron) grains<br>(a) (b) (c) (d) finely intergrown (2-10 micron range)<br>(c) (d) 5% in total, alligned<br>(1) veins and blebs (same size range as above) } 1/2%<br>(2) scattered 1-5 micron irregular grains ) } |
| Type 5 (47.2% of sample population) | (a) quartz<br>(b) Fe(Mn) chlorite<br>(c) KFe(Mg) mica<br>(d) KFeMg mica<br><br>(1) Ti oxide (creamy grey)<br>(2) Fe oxide ("red gel")<br>(3) pyrite<br>(4) manganite<br>(5) MnTi oxide (pyrophanite)<br>(6) psilomelane | (a) (b) (c) or (d) finely intergrown at 1-10 micron level<br>-(a) is fine mozaic silica<br>-(a)/(b) sometimes present as larger (30-50 micron) grains/"fans"<br>-the micas generally (only 4 grains aren't) are aligned<br>-(b) one fragment contains a chlorite vein (10 micron wide)<br>(1) all the fragments contain $\leq$1/2% of irregular grains (<1-20 micron in size)<br>(2) (3) 3 fragments contain euhedral to subhedral grains (10-50 micron across) sometimes containing pyrite cores<br>(4) 3 fragments contain thin manganite veins (1-5 micron) and one fragment contains traces of manganite blebs (1-10 micron across)<br>(5) 1 fragment contains a small irregular series of veins (1-2 micron across)<br>(6) 2 fragments contain psilomelane veins (2-10 micron across) |
| Type 6 (0.9% of sample population | (a) Na-spar<br>(b) KFeAlSi<br><br>(1) Fe(Mn) oxide (magnetite)<br><br>(2) psilomelane (Ca)<br>(3) hematite | (1) 1% Mn very minor, larger grains (100-200 micron) irregular<br>(2) (3) fine (5-30 micron) irregular grains (blebs) intergranular with gangue, 5-10% of each fragment<br>(a) (b) intergrown at 5-40 micron level - albite often larger equant grains |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 7 (4.4% of sample population) | (a) K(Mg,Fe) mica<br>(b) quartz<br>(c) Na-spar<br>(d) Fe chlorite<br><br>(1) Ti,Fe Oxide<br>(2) Fe oxide<br>(3) Ti oxide | (a) (b) (c) (d) finely intergrown (5-15 micron)<br>(d) trace only<br>(1) irregular grains (5-20 micron) generally smaller<br>(2) (5) (5-10 micron range) irregular grains<br>(2) sometimes large 50-60 micron |
| Type 8 (3.5% of sample population | (a) K-spar/Na-spar (one or the other)<br>(b) quartz<br>(c) Fe(Mn) chlorite (sometimes no Mn or more Mn than Fe) (sometimes minor Ca)<br>(d) FeKAlSi<br>(e) KFe(Mn)Mg mica<br>(f) K(Fe,Mg) mica<br>(g) apatite<br><br>(1) hematite<br>(2) psilomelane (minor Ca)<br>(3) manganite | (a) (c) (d) finely intergrown (2-10 micron level) with larger (10-25 micron) grains of quartz (b)<br>or (b) (e) (c) finely intergrown (2-5 micron level)<br>or (a) (c) (minor Ca) (b) (f) finely intergrown (2-5 micron)<br>or (b) (c) (g) finely intergrown (2-10 micron), (g) apatite only traces<br>(1) small irregular to acicular grains (1-5 micron)<br>-from 5 to 20% of fragment<br>-layering usually evident-defined by concentrations of hematite grains<br>-some larger (25-50 micron) irregular grains may be present (rare)<br>(2) (3) one fragment also contains 2-3% manganite blebs (15-40 micron) and psilomelane blebs (15-60 micron)<br>(2) one fragment also contains psilomelane blebs (15-40 micron) and 2 massive blocky psilomelane veins (5-20 micron across)<br>(2) (3) one fragment contains large psilomelane semi equant blebs intergrown with the hematite and gangue, and a fine manganite vein (1-5 micron) |
| Type 9 (1.8% of sample population) | (a) quartz<br><br>(b) Na-spar<br>(c) Fe chlorite<br><br>(1) TiO<br>(2) FeO | (a) (b) (c) fine to med. grained mozaic texture between spar and quartz<br><br>(1) (2) fine (1-10) micron) |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 10 (7.9% of sample population | (a) Na-spar<br>(b) quartz<br>(c) KFeMg mica<br>(d) Fe chlorite<br>(e) K(Fe,Mg)AlSi<br><br>(1) Fe oxide (magnitite)<br>(2) Fe oxide (hematite)<br>(3) Ti oxide<br>(4) zircon<br>(5) MnFe oxide (jacobsite)<br>(6) FeO<br>(7) CeLaNdSZrSi | (a) (b) large grains (equant) (5-40 micron) 45%<br>(c) (d) (e) finely intergrown (5-15 micron)<br>(d) very rare, more abundant as large fans (20-40 micron)<br>(1) (2) as large blebs or veins ( 10-60 micron wide) <1/2%<br>(3) large and small irregular grains 2-60 micron generally 2-5<br>(4) rare grains 5-10 micron<br>(5) <1/2% small equant grains (1-5 micron)<br>(7) small grains (trace!!) (1-5 micron) |
| Type 11 (7.9% of sample population) | (a) quartz<br>(b) K(FeMg) mica<br>(c) Fe(Mn)KMg mica<br><br>(1) Ti oxide | (a) ]<br>(b) ] finely intergrown at 1-5 micron<br>(c) ] trace only maybe 5%<br>(1) small irregular grains (1/2-2 micron) <1/2% |
| Type 12 (2.6% of sample population) | (a) Na-spar<br>(b) FeMnK mica<br>(Mn minor sometimes)<br>(c) quartz<br><br>(1) manganite<br>(2) Fe oxide (hematite)<br>(3) pyrolusite | (a) (b) (c) intergrown at 2-8 micron level<br>-(a) (c) : (b) = 1:1 (approximately)<br>(1) all contain from 10-30% manganite (with minor Ca) as equant blebs 5-15 micron across, often a bit spongy<br>(2) minor hematite usually as small (1-5 micron) grains<br>-one grain ( 25 micron across) anhedral observed<br>(3) very minor pyrolusite may be present in manganite (1) blebs |
| Type 13 (0.9% of sample population | (a) quartz<br>(b) Fe(Mn,K) chlorite<br>(c) K(Fe) mica<br>(d) Ca phosphate (apatite)<br><br>(1) Fe oxide<br>(2) Ti oxide | (a) (b) (c) finely intergrown 5-10 micron range<br>(d) 1 equant grain 15 micron across<br>(1) (2) small (1-5 micron) irregular grains <1/2% |

| Fragment Type | Mineral Assemblage | Descriptive Details |
|---|---|---|
| Type 14 (1.8% of sample population) | (a) quartz<br>(b) K(Fe,Mg) mica<br>(c) KFeMg mica<br><br>(1) Ti oxide<br>(2) TiFe oxide (ilmenite)<br>(3) CoNdZrBaSmSi | (a) (b) (c) intergrown at (5-15 micron)<br>(1) 1-10 micron<br>(2) often acicular (2-5 micron)<br>(3) 2 micron across |
| Type 15 (1.8% of sample population) | (a) quartz<br>(b) K(FeMg) mica<br>(c) Fe chlorite<br><br>(1) Fe oxide<br>(2) zircon | (a) (b) (c) intergrown at 10-20 micron range<br>(a) 85%<br>(b) 10% - of interstitial material (25% of fragment)<br>(c) 5%<br>(a) large 0.5-1 mm size rounded grains<br>(1) 4 large irregular grains 150 micron<br>(2) large grain 25 micron |

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# PART C: CHEMICAL ANALYSIS OF NEW BRUNSWICK MANGANESE DEPOSITS

CONTENTS


| | Page |
|---|---|
| A) Introduction | 1 |
| B) Experimental | 1 |
| 1) Sample preparation and Acid Digestion | 1 |
| 2) Pulverizing | 1 |
| 3) Hydrofluoric - aqua regia digestion | 2 |
| 4) Determination of the elements | 2 |
| 5) Determination of Cu, Co, Cr, Ni and Zn | 3 |
| 6) Determination of Mn, Fe, Al, and Ti | 3 |
| 7) Determination of Ca and Mg | 3 |
| 8) Determination of Na and K | 4 |
| 9) Determination of silver (assay method) | 4 |
| 10) Determination of sulphur | 5 |
| i) Principle | 5 |
| ii) Procedure | 6 |
| 11) Determination of Phosphorus | 7 |
| 12) Discussion of results of Chemical elements | 11 |
| C) Characterization of Manganese Oxidation states | 15 |
| D) Introduction | 15 |
| E) Literature Search for chemical reactions of Manganese and analytical methods relevant to characterization of Manganese oxidations states. | 20 |

| | Page |
|---|---|
| F) Experimental | 25 |
| i) Method employed in the determination of Manganese (IV) | 25 |
| Principle | 25 |
| Procedure | 25 |
| ii) Method used in determination of Manganese (III) | 26 |
| Principle | 26 |
| Procedure | 27 |
| iii) Method used in determination of Manganese (II) | 27 |
| Principle | 27 |
| Procedure | 28 |
| IV) Method for direct titrimetric determination of Manganese (II) | 31 |
| Principle | 31 |
| Procedure | 31 |
| Discussion of results of manganese oxidation states | 33 |
| References cited | 35 |

# PART C: CHEMICAL ANALYSIS OF NEW BRUNSWICK MANGANESE DEPOSITS

## A) INTRODUCTION

Chemical analyses were performed by Atlantic Analytical Services Ltd. The eight (8) samples were each weighed out in triplicate, digested in hydrofluoric acid (HF) - aqua regia total dissolution media and the following chemical elements were determined using atomic absorption spectrophotometry: Mn, Fe, Ca, Mg, Al, Ti, K, Na, Cu, Co, Cr, Ag, Zn and Ni. Phosphorus was determined colorimetrically and sulphur was analyzed by a gravimetric method.

The various oxidation states in which manganese exists in the New Brunswick manganese deposits were determined titrimetrically using established analytical methods. Details of each method used are included in this report.

## B) EXPERIMENTAL

### Sample Preparation and Acid Digestion

1) Pulverizing: Eight (8) manganese samples of approximately 2 Kg each were received from R.P.C. already crushed to about -18 mesh fraction. The samples were pulverized to -80 mesh, each sample was placed on a plastic sheet and was rolled from corner to corner for a minimum of 14 times to ensure homogeneity.

2) Hydrofluoric - Aqua regia Digestion

A portion of sample (1.0000g) was accurately weighed in triplicate and placed into clean teflon beakers. Freshly prepared aqua regia (5 ml) was added to oxidize organic matter and hydrofluoric acid (10 ml) was added. The beakers were covered with teflon lids and the samples were slowly heated to dryness on the sandbath. The residues were allowed to cool and the process was repeated using hydrofluoric acid ( 5 ml) and heating to dryness until complete dissolution of the manganese minerals was achieved. Aqua regia (10 ml) was added to each cool residue and dissolution was allowed to proceed to completion. The solutions were made to 100 ml using distilled water.

3) Determination of the Elements

Except for phosphorus and sulphur, all the elements were determined using a Perkin Elmer 2380 flame Atomic Absorption Spectrophotometer. Internal reference standards and reagent blanks were made up in appropriate concentrations of digestion acid and were employed in the calibration of the instrument. Each sample was read four times using the lower and higher reference standards to bracket each sample reading and a reagent blank was read after each sample. Depending upon the stability of the instrument and the specific element being determined, the calibration curve was checked after 2-5 samples. In the case of manganese, an external reference material was analyzed, in addition

to the internal reference materials to monitor analytical precision and accuracy.

4) Determination of Cu, Co, Ni, Cr, and Zn

These elements were determined (in parts per million) directly on the HF-aqua regia solutions. The operating conditions under which these elements were analyzed are summerized in Table 1. No interference problems have been reported for these elements when analyzed by atomic absorption.

5) Determination of Mn, Fe, Al, and Ti

The HF-aqua regia solutions were diluted 1:10 and the acid concentrations were adjusted to match those of reference standards. Mn, Fe, Al and Ti were analyzed and the data were reported in "percent" as a unit of concentration. The operating conditions of the Atomic Absorption spectrophotometer, the anticipated interference problems and their effects on the quality of analytical data, and the methods employed to minimize them are briefly outlined in Table 1.

6) Determination of Ca and Mg

In the air-acetylene flame, Ca slightly ionizes and Si, Al, $PO_4^{=}$, $SO_4^{=}$, Ti and Zr tend to depress the sensitivity of calcium and magnesium. To rectify these interference problems a portion (10 ml) of the HF-aqua regia solution was pipetted into a

100 ml volumetric flask and 20 ml of 1% Lanthanum Oxide solution and 10 ml of aqua regia were added. The solutions were cooled; made to 100 ml mark with distilled water and Ca and Mg were determined by atomic absorption operating under the conditions outlined in Table 1. Reference standards and reagent blanks were made exactly the same way as the samples and were used to calibrate the instrument.

7) Determination of Na and K

For each sample, two portions of 10 mls each were pipetted from the HF-aqua regia solutions and were placed into 100 ml volumetric flasks. To the first portion, 1 ml of 10,000 ppm $Na^+$ solution was added. To the second portion 1 ml of 10,000 ppm $K^+$ was added. Aqua regia (10 ml) was added to both portions and the solutions were made to volume. Potassium was determined on the first solution and sodium was determined on the second solution using atomic absorption and the internal reference standards and reference blanks made with appropriate concentrations of alkali and aqua regia. Addition of alkali solutions was intended to minimize ionization interferences of sodium and potassium in the air-acetylene flame (see Table 1 for details).

8) Determination of Silver (Assay Method)

A small part of sample (1.0000 g) was weighed in triplicate and placed into 250 ml beakers. Concentrated

hydrochloric acid (15 ml) was added and the samples were slowly heated to near dryness. The samples were allowed to cool and additional concentrated hydrochloric acid (10 ml) and concentrated nitric acid (25 ml) were added. The samples were slowly heated until the volume in the beaker was less than 25 mls. The samples were allowed to cool and were quantitatively transferred into 100 ml volumetric flasks. Concentrated hydrochloric acid (20 ml) was added and the solutions were made to volume with distilled water. Silver was determined by atomic absorption in ounces/tonne using electronic background corrector. (See Table 1)

Calculation: 1 ppm = 0.0292 oz/t

9) Determination of Sulphur

i) Principle:

The samples were analyzed for sulphur content using the method proposed by Lunge in which reversed aqua regia is used to oxidize sulphur to sulphate. The reaction must be carried out in the cold because sulphur may precipitate from hot solutions prior to oxidation. After dissolution, the nitric acid solution is evaporated several times on the waterbath; the nitrates are decomposed; silicic acid is precipitated and iron (III) is removed from the filtrate using ammonia solution. The sulphate in the samples is precipitated as Barium sulphate.

ii) Procedure:

An accurately weighed portion of sample (1.0000 g) was placed into 250 ml beaker and cooled with ice-water. Freshly prepared and ice-cooled reverse aqua regia (10 mls) was added to the sample in the beaker and the mixture was allowed to stand overnight in ice-water. The beaker was placed into a water bath and heated slowly until no more brown fumes were liberated. It was then evaporated to dryness on a steam bath. The evaporation was repeated two times using 10 ml of hydrochloric acid (1:1). After adding 1 ml of concentrated hydrochloric acid to the cool residue, it was dissolved in 100 ml of hot distilled water and filtered through an ash-free filter paper making sure to wash the residue thoroughly with distilled water.

Iron (III) ions were precipitated from the hot filtrate using 20 ml of 10% ammonia.. The mixture was heated on a water bath for 30 minutes, filtered and the residue washed with hot water. The residue was washed back into the beaker dissolved in a small volume of 10% hydrochloric acid and iron (III) was reprecipitated with ammonia. The two filtrates were mixed and heated to remove excess ammonia. A few drops of methyl orange indicator were added and the solution was neutralized with hydrochloric acid and then acidified with 1 ml of concentrated hydrochloric acid. The solution was diluted to about 400 ml and heated to boiling. A warm solution of 10% barium chloride solution (20 mls) was added to the boiling sulphate

solution with stirring. The mixture was allowed to stand overnight, filtered on ash-free filter paper and the residue washed until chloride could no longer be detected in the washings. The filter paper and contents were placed in a pre-weighed crucible and heated at 800$^{o}$C for one hour. The crucible and contents were weighed, the amount of barium sulphate computed, and the sulphur content of samples were calculated using the following factor:

Stoichiometric factor: $S/BaSO_4 = 0.13737$

10) Determination of Phosphorus

A portion of sample (5.000 g) was weighed out in triplicate into 250 ml beakers. Concentrated nitric acid (20 mls) and perchloric acid (15 mls) were added and the samples were digested on a hot plate till heavy fumes of perchloric acid began to appear and the sample solutions turned greenish or clear. In some cases, more nitric acid (10 mls) and perchloric acid (5 mls) were added and the samples heated and the process was repeated until the manganese minerals dissolved.

The solutions were transferred into 100 ml volumetric flasks and made to volume using distilled water. The samples were allowed to stand overnight to allow particles to settle. Eight (8) mls of clear solution of sample were pipetted into a test tube and 2 ml of mixed reagent, prepared by mixing equal volumes of ammonium vanadate and ammonium molybdate, were added. The samples were thoroughly shaken; allowed to sit for 15 minutes

and phosphorus was corolimetrically determined on spec 20 at 400 nm. Reagent blanks containing two mls of mixed reagent were used to calibrate the instrument. Using standard solutions of known phosphorus content, a graph showing absorbance and corresponding phosphorus concentrations was constructed. This graph was used to determine the phosphorus content in the samples by measuring their absorbances.

TABLE 1

| Element | Wavelength (nm) | Flame Type | Interference | Method used to minimize interference |
|---|---|---|---|---|
| Mn | 403.1 | Air-acetylene oxidizing (lean, blue) | None | None |
| Fe | 248.3 | Air-acetylene very lean (hot) falme | Nitric acid and nickel reduce sensitivity | Used very lean (hot) flame |
| Ca | 422.7 | Air-acetylene oxidizing (lean blue) | Si, Al, Ti, Zr, $PO_4^{2-}$, $SO_4^{2-}$ depress sensitivity | Added lanthanum oxide solution to sample solutions and standards |
| Mg | 285.2 | Air-acetylene oxidizing(lean blue) | Si, Al depress absorption | Added lanthanum oxide solution |
| Al | 309.3 | Nitrous oxide-acetylene (reducing rich, red) | Fe, depresses sensitivity; Ti increases sensitivity Al ionizes | No special corrective measures were taken. Al data may reflect minor errors from ionization effects. |
| K | 766.5 | Air-acetylene oxidizing (lean ,blue) | Ionization | added 1ml of 10,000 ppm $Na^+$ solution |
| Na | 589.6 | Air-acetylene oxidizing (lean, blue) | Ionization | Added 1 ml of 10,000 ppm K+ solution |
| Ti | 365.5 | Nitrous oxide-acetylene. Reducing (rich, red) | Sensitivity increased by Fe and Al | Data may reflect interference effects from Co, K, Mn, Na, Cn, Ca, Cr, Li, Mg, Mo, Cd, Zn, Ni, Pb. |

TABLE 1 con't

| | | | | |
|---|---|---|---|---|
| Cu | 324.8 | Air-acetylene oxidizing (lean, blue) | None | None |
| Co | 240.7 | Air-acetylene oxidizing (lean, blue) | None | None |
| Ni | 232.0 | Air-acetylene oxidizing (lean, blue) | None | None |
| Cr | 357.9 | Air-acetylene Reducing (rich, yellow) | Sensitivity supressed by Fe and Ni | Used lean, flame to minimize interference from Fe and Ni. |
| Zn | 213.9 | Air-acetylene oxidizing (lean, blue) | None | None |
| Ag | 328.1 | Air-acetylene oxidizing | Background effects | Used background corrector |

11) Discussion of Results of Chemical Elements

The analytical data on the 16 chemical elements determined on each sample are given in Table 2. The data indicate that the two deposits sampled have rather low concentration levels of manganese. The North Hartford deposit has manganese concentrations ranging from an average of 2.59% to 3.82%. These low manganese values are associated with relatively high concentrations of total iron and aluminium. In the Plymouth deposit however, the concentrations of manganese rise to a maximum average of 9.97%; total iron exceeds 17% but total aluminum levels appears to be similar to those encountered in samples from North Hartford deposit. It was felt that perhaps the HF-aqua regia dissolution media did not effectively dissolve all the manganese in the sample. To check this, a reference sample was obtained from R.P.C. and was subjected to similar acid digestion procedure as the samples. An average of 5.13% Mn was obtained and this compares to 5.11% Mn reported by R.P.C. Sample number P5 from Plymouth deposit had very low manganese concentrations (0.46%), moderate total iron values (3.17%) and very high calcium concentrations (12.49%). The high calcium content plus the effervesence of the samples with acid indicate high calcium carbonate content.

It was noted during sample preparation that the 8

manganese samples particularly NH3, P1, P2, P3, P4 and P5 contained substantial quantities of mud and soil. Owing to this dilution of the samples it is conceivable that the actual concentrations of manganese may indeed be higher than those obtained in this study.

TABLE 2 : Analytical Data of Trace and Minor Elements in New Brunswick Manganese Deposits.

| Sample # | ppm Cu | ppm Co | ppm Ni | ppm Cr | ppm Zn | oz/t Ag | P | S |
|---|---|---|---|---|---|---|---|---|
| NH1 | 81 | 174 | 150 | 268 | 137 | LO.05 | 0.043 | LO.01 |
| NH1 | 80 | 174 | 150 | 269 | 138 | LO.05 | 0.041 | LO.01 |
| NH1 | 83 | 174 | 151 | 264 | 136 | LO.05 | 0.037 | LO.01 |
| NH2 | 43 | 172 | 135 | 236 | 111 | LO.05 | 0.041 | LO.01 |
| NH2 | 43 | 173 | 135 | 239 | 114 | LO.05 | 0.041 | LO.01 |
| NH2 | 45 | 173 | 135 | 239 | 111 | LO.05 | 0.040 | LO.01 |
| NH3 | 46 | 114 | 116 | 240 | 112 | LO.05 | 0.020 | LO.01 |
| NH3 | 46 | 116 | 112 | 239 | 112 | LO.05 | 0.021 | LO.01 |
| NH3 | 47 | 118 | 113 | 238 | 112 | LO.05 | 0.016 | LO.01 |
| P1 | 46 | 137 | 114 | 199 | 89 | LO.05 | 0.119 | LO.01 |
| P1 | 46 | 134 | 115 | 204 | 90 | LO.05 | 0.116 | LO.01 |
| P1 | 46 | 138 | 115 | 203 | 89 | LO.05 | 0.108 | LO.01 |
| P2 | 80 | 162 | 142 | 205 | 98 | LO.05 | 0.097 | LO.01 |
| P2 | 80 | 163 | 143 | 206 | 98 | LO.05 | 0.087 | LO.01 |
| P2 | 81 | 164 | 145 | 203 | 97 | LO.05 | 0.071 | LO.01 |
| P3 | 37 | 184 | 126 | 222 | 97 | LO.05 | 0.099 | LO.01 |
| P3 | 37 | 185 | 126 | 221 | 96 | LO.05 | 0.108 | LO.01 |
| P3 | 37 | 185 | 126 | 223 | 95 | LO.05 | 0.101 | LO.01 |
| P4 | 89 | 187 | 144 | 218 | 88 | LO.05 | 0.425 | LO.01 |
| P4 | 86 | 187 | 143 | 215 | 86 | LO.05 | 0.400 | LO.01 |
| P4 | 89 | 187 | 143 | 211 | 88 | LO.05 | 0.388 | LO.01 |
| P5 | 33 | 80 | 135 | 238 | 76 | LO.05 | 0.025 | LO.01 |
| P5 | 33 | 79 | 132 | 238 | 76 | LO.05 | 0.019 | LO.01 |
| P5 | 33 | 79 | 135 | 237 | 77 | LO.05 | 0.012 | LO.01 |

TABLE 2: Analytical Data of Major Elements in New Brunswick Manganese Deposits

| Sample # | % Mn | % Fe | % Ca | % Mg | % Al | % K | % Na | % Ti |
|---|---|---|---|---|---|---|---|---|
| NH1 | 3.80 | 8,66 | 0.21 | 1.79 | 9.48 | 2.77 | 0.18 | 0.56 |
| NH1 | 3.78 | 8.65 | 0.24 | 1.77 | 9.66 | 2.78 | 0.18 | 0.57 |
| NH1 | 3.87 | 8.62 | 0.26 | 1.79 | 9.40 | 2.76 | 0.18 | 0.57 |
| NH2 | 3.67 | 6.72 | 0.58 | 1.97 | 8.14 | 2.39 | 0.18 | 0.43 |
| NH2 | 3.67 | 6.71 | 0.61 | 1.97 | 7.86 | 2.36 | 0.18 | 0.45 |
| NH2 | 3.71 | 6.70 | 0.65 | 1.95 | 8.16 | 2.37 | 0.18 | 0.44 |
| NH3 | 2.56 | 4.17 | 0.15 | 1.81 | 8.50 | 2.79 | 0.17 | 0.42 |
| NH3 | 2.61 | 4.12 | 0.15 | 1.84 | 8.45 | 2.84 | 0.17 | 0.40 |
| NH3 | 2.61 | 4.21 | 0.16 | 1.83 | 8.27 | 2.93 | 0.17 | 0.40 |
| P1 | 7.36 | 9.34 | 3.85 | 1.45 | 6.31 | 1.96 | 0.18 | 0.37 |
| P1 | 7.37 | 9.28 | 3.85 | 1.47 | 6.20 | 1.96 | 0.18 | 0.35 |
| P1 | 7.38 | 9.35 | 3.82 | 1.45 | 6.33 | 1.96 | 0.18 | 0.39 |
| P2 | 8.49 | 8.42 | 2.87 | 1.41 | 7.77 | 1.72 | 0.19 | 0.43 |
| P2 | 8.44 | 8.40 | 2.91 | 1.47 | 7.86 | 1.74 | 0.19 | 0.42 |
| P2 | 8.47 | 8.38 | 2.85 | 1.47 | 7.86 | 1.76 | 0.19 | 0.41 |
| P3 | 7.06 | 11.60 | 0.67 | 1.62 | 9.49 | 1.75 | 0.19 | 0.50 |
| P3 | 7.06 | 11.69 | 0.62 | 1.62 | 9.37 | 1.74 | 0.19 | 0.48 |
| P3 | 7.06 | 11.64 | 0.63 | 1.59 | 9.49 | 1.75 | 0.19 | 0.44 |
| P4 | 9.96 | 17.11 | 0.39 | 1.23 | 7.76 | 1.66 | 0.16 | 0.19 |
| P4 | 9.98 | 17.12 | 0.38 | 1.26 | 7.47 | 1667 | 0.16 | 0.19 |
| P4 | 9.97 | 17.15 | 0.37 | 1.26 | 7.54 | 1.66 | 0.16 | 0.19 |
| P5 | 0.46 | 3.15 | 12.54 | 2.13 | 6.05 | 1.43 | 0.18 | 0.23 |
| P5 | 0.45 | 3.18 | 12.47 | 2.13 | 6.33 | 1.42 | 0.18 | 0.20 |
| P5 | 0.47 | 3.19 | 12.47 | 2.14 | 6.23 | 1.41 | 0.18 | 0.21 |

## C) CHARACTERISATION OF MANGANESE OXIDATION STATES

## D) INTRODUCTION

Studies of the chemistry of transition metals indicate that manganese can exhibit a maximum range of oxidation states from manganese (-III) to manganese (VII) (Table 3). In general, however, the manganese compounds commonly encountered in laboratory studies have the positive oxidation states II, III, IV, and VII. In naturally occurring geologic materials the number of manganese species is further reduced because the existing Eh-pH conditions and the chemistry of aqueous systems place definite limitations on the stability and occurrence of certain manganese oxidation states. For example, in alkaline solutions of low oxidizing power, solid $Mn(OH)_2$ predominates; in acid and reducing media Mn (II) predominates; $Mn(OH)_3$ - becomes important only in very basic solutions; in solutions of moderate oxidizing power solid $MnO_2$ is the predominant species at au pH values; $MnO_4^{2-}$ can be obtained in strong alkalis; Mn (III) can be obtained in very strong acids; in strongly oxidizing media $MnO_4$ predominates and $MnO_3$ is never predominant but occurs in high pH and moderate oxidizing media. Table 4 shows the potentials for the formation of the various oxidation states of manganese and Fig 1 is a pH-potential diagram illustrating the regions in which various forms of manganese species predominate (Kolthoff et al., 1961).

TABLE 3:

Some Oxidation States of the Metals of the First Transition Series (from Huheey, 1972)

| Oxidation number | Group IIIB | IVB | VB | VIB | VIIB | VIIIB | | | IB | IIB |
|---|---|---|---|---|---|---|---|---|---|---|
| VII | | | | | $[MnO_4]^-$ | | | | | |
| VI | | | | $[CrO_4]^{-2}$ | $[MnO_4]^{-2}$ | $[FeO_4]^{-2}$ | | | | |
| V | | | $[VO_4]^{-3}$ | $[CrO_4]^{-3}$ | $[MnO_4]^{-3}$ | $[FeO_4]^{-3}$ | | $[NiF_6]^{-2}$ | | |
| IV | | $TiO_2$ | $[VOF_4]^{-2}$ | $[CrO_4]^{-4}$ | $MnO_2$ | $[FeO_4]^{-4}$ | $[CoF_6]^{-2}$ | $[NiF_6]^{-3}$ | $[CuF_6]^{-3}$ | |
| III | $Sc^{+3}$ | $Ti^{+3}$ | $V^{+3}$ | $Cr^{+3}$ | $[Mn(CN)_6]^{-3}$ | $Fe^{+3}$ | $[Co(CN)_6]^{-3}$ | $Ni^{+2}$ | $Cu^{+2}$ | $Zn^{+2}$ |
| II | | $TiCl_2$ | $V^{+2}$ | $Cr^{+2}$ | $Mn^{+2}$ | $Fe^{+2}$ | $Co^{+2}$ | | $[Cu(CN)_2]^-$ | |
| I | | | | $[Cr(dipy)_3]^+$ | $[Mn(CN)_6]^{-5}$ | | $[Co(dipy)_3]^+$ | | | $[Zn(dipy)_3]$ |
| 0 | | $[Ti(dipy)_3]$ | $[V(dipy)_3]$ | $[Cr(dipy)_3]$ | $[Mn(dipy)_3]$ | $[Fe(dipy)_3]$ | $[Co(dipy)_3]$ | $[Ni(dipy)_3]$ | | |
| −I | | | $[V(dipy)_3]^-$ | $[Cr(dipy)_3]^-$ | $[Mn(dipy)_3]^-$ | $[Fe(dipy)_3]^-$ | $[Co(CO)_4]^-$ | | | |
| −II | | | | $[Cr(dipy)_3]^{-2}$ | | $[Fe(CO)_4]^{-2}$ | | | | |
| −III | | | | $[Cr(dipy)_3]^{-3}$ | $[Mn(NO)_3CO]^a$ | | | | | |

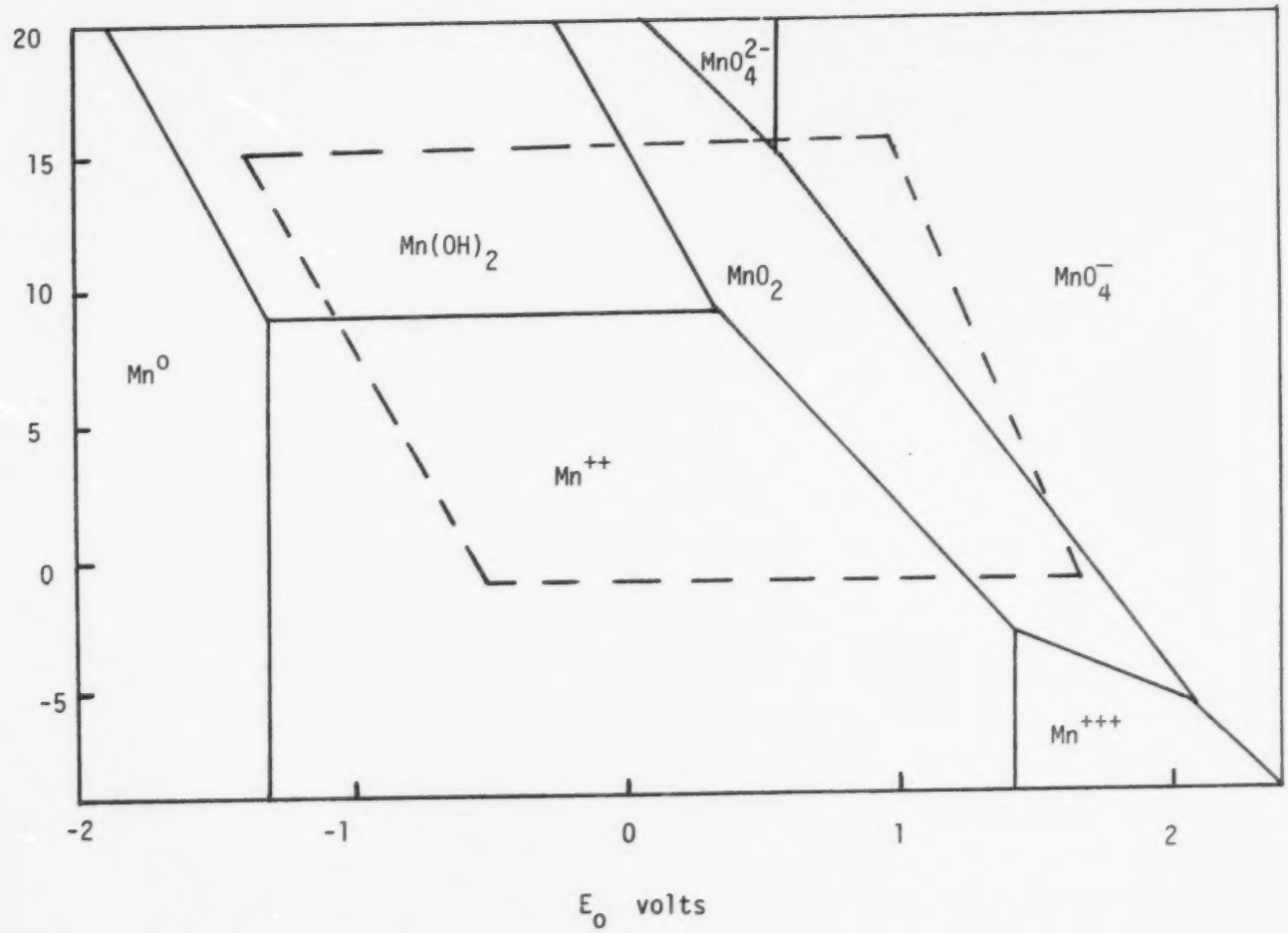
[a]Oxidation state of manganese based on assumption of nitrosyl = $NO^+$

The foregoing paragraphs serve to indicate the problems that may be encountered when samples containing manganese are dissolved in solutions especially when the various oxidation states are sought in the form in which they occurred in the original solid samples.

TABLE 3: POTENTIALS FOR THE FORMATION OF THE VARIOUS OXIDATION STATES OF MANGANESE (Kolthoff et al. 1961).

| Oxidation State Formed | Half Reaction | $E^o$ |
|---|---|---|
| 0 | $MnO_2$ (s) + $4H^+$ + $4\bar{e}$ = Mn (s) + $2H_2O$ | +0.205 |
| +2 | $MnO_2$ (s) + $4H^+$ + $2\bar{e}$ = $Mn^{++}$ + $2H_2O$ | +1.23 |
| +2 | $MnO_2$ (s) + $3H^+$ + $2\bar{e}$ = $MnOH^+$ + $H_2O$ | +0.91 |
| +2 | $MnO_2$ (s) + $2H^+$ + $2\bar{e}$ = $Mn(OH)_2$ (s) | +0.77 |
| +2 | $MnO_2$ (s) + $2H^+$ + $2\bar{e}$ = $Mn(OH)_2$ (aq) | +0.60 |
| +2 | $MnO_2$ (s) + $H^+$ + $H_2O$ + $2\bar{e}$ = $Mn(OH)_3^-$ | +0.20 |
| +3 | $MnO_2$ (s) + $4H^+$ + $\bar{e}$ = $Mn^{+++}$ + $2H_2O$ | +0.95 |
| +3 | $MnO_2$ (s) + $H^+$ + $H_2O$ + $2\bar{e}$ = $Mn(OH)_2$ (s) | +0.59 |
| +5 | $MnO_2$ (s) + $H_2O$ = $MnO_3^-$ + $2H^+$ + $\bar{e}$ | -2.5 |
| +6 | $MnO_2$ (s) + $2H_2O$ = $MnO_4^{2-}$ + $4H^+$ + $2\bar{e}$ | -2.26 |
| +7 | $MnO_2$ (s) + $2H_2O$ = $MnO_4^-$ + $4H^+$ + $3\bar{e}$ | -1.695 |

Figure 1 pH- potential diagram for Manganese showing the regions in which the various forms of manganese predominate (Kolthoff et al, 1961)



# LITERATURE SEARCH FOR CHEMICAL REACTIONS OF MANGANESE AND ANALYTICAL METHODS RELEVANT TO CHARACTERIZATION OF MANGANESE OXIDATION STATES

A comprehensive literature search was conducted for this project in order to obtain information on the existing analytical methods for characterization of manganese oxidation states in geologic materials. The computer facilities and other resources in the libraries in the two campuses of the University of New Brunswick in Fredericton and Saint John were fully utilized. The literature showed that most of the analytical methods (Morgan and Stumm, 1965) determine the total concentration of manganese in samples and are not concerned with distinguishing and determining quantitativley the various oxidation states of manganese; an objective which this project intends to accomplish. Few attempts have been made to measure the average oxidation state of manganese in sediments and nodules (e.g. Sevast'yanov, 1966; Grill et. al. 1968, 1969; Manheim, 1965; Kessick et. al. 1972; and Freeman and Chapman, 1971.) Most methods encountered in the literature surveyed are based on wet chemical principles involving reduction - oxidation titrimetric approach after stabilization and/or isolation of the required manganese species (Martell and Calvin, 1953; Welcher, 1958; Bernard et al. 1957; Taimmi et al., 1957; Fyfe 1949). Methods based on instrumental techniques to characterize manganese oxidation states are very scarce in the literature. Wakeham and Carpenter (1974) identified manganese (II) in nodules using electron spin resonance spectroscopy (ESR), however, they

concluded that it must be present in only trace amounts. Dillard et al. (1982) examined four samples of manganese nodules using x-ray photo-electron spectroscopy (XPS) and could not identify any manganese below oxidation state IV. Lenglet et al. (1985) attempted to characterize the oxidation states of manganese in manganite samples using XPS and were only able to tentatively conclude that " it appears that manganese is in +2, +3, and +4 oxidation states." Owing to the proven reliability of the titrimetric methods in determination of oxidation states of manganese, and in view of the fact that instrumental methods are in early developmental stages and are not yet able to give reliable and definitive results, it was decided that titrimetric methods be used in this work.

The following chemical reactions which are sensitive to particular oxidation states of manganese were identified as potential analytical tools for characterization of oxidation states.

Manganese (II)

Manganese (II) instantaneously reacts with permanganate in neutral solutions according to the following reaction:

$$Mn\ (II) + MnO_4^- = Mn\ (III) + MnO_4^{2-}$$

Hence manganese (II) ion may be determined directly by titrating manganese (II) solutions in neutral pyrophosphate solutions with standard permanganate (Lingane and Karplus, 1946).

$$4\ Mn\ (II) + MnO_4^- + 8H^+ + 15\ (H_2P_2O_7)^{2-} = 5\ (Mn\ (H_2P_2O_7)_3)^{3-} + 4H_2O$$

Manganese (II) may also be titrated directly with disodium EDTA in ammoniacal tartrate solution containing ascorbic acid using Eriochrome Black T as indicator (Welcher, 1958).

Manganese (II) reacts with 1-(2-Pyridylazo)-2-Napthol (PAN) at pH 9 to form a red complex into chloroform or ether. The ether extract shows absorbance maxima at 530 and 562 mμ and can be utilized as a colorimetric method for determination of manganese (II) (Montagut - Buscus et al. 1967).

Manganese (III)

In the absence of a complexing agent manganese (III) is a very strong unstable oxidant (Latimer, 1952).

$$Mn\ (III) + \acute{e} = Mn\ (II) \qquad E = 1.5V$$

However, in the presence of a complexing agent such as pyrophosphate in acid solution, manganese (III) is greatly stabilized and can be directly determined titrimetrically by reacting with standard potassium iodide solution and titrating the liberated iodine with standard solution of thiosulphate.

$$Mn\ (H_2P_2O_7)_3^{3-} + 2H^+ + \acute{e} = Mn\ (H_2P_2O_7)_2^{2-} + H_4P_2O_7 \quad E^o = 1.15V$$

$$2Mn\ (III) + 2I^- = I_2 + 2Mn\ (II)$$

Manganese (III) forms a green complex in the presence of

triethanolamine which has a strong absorption band maximum at 438 mμ and has been used to determine manganese colorimetrically (Nightingale, 1959)

Manganese (IV)

Manganese (IV) oxide reacts with concentrated hydrochloric acid evolving chlorine gas.

$$MnO_2 + 4HCL = Mn\ (II) + 2CL_2 + 2H_2O$$

The evolved chlorine gas can be titrated with standard thiosulphate solution and the amount of manganese (IV) can be calculated (Vogel, 1961).

Manganese (IV) as $MnCL_2$ reacts with acetylacetone to form Mn (III) complex and a chlorinated derivative of acetylacetone that will oxidize iodine solution in acid media. The resulting iodine can be titrated with thiosulphate and the amount of manganese (IV) originally present can be obtained (Fyfe, 1949).

$$MnO_2 + 4HCL = MnCL_4 + 2H_2O$$

$$2MnCL_4 + x\ (CH_3COCH_2COCH_3) = 2Mn\ CL_3\ (CH_3COCH_2COCH_3)\ x - 1 +$$

$$CH_3COCHCLCOCH_3 + HCL$$

$$CH_3COCHCLCOCH_3 + 2KI = CH_3COCH_2COCH_3 + HCL + I_2$$

Manganese (IV) oxide reacts with hydrogen peroxide in the presence of dilute sulphuric acid to give oxygen gas as one of the products.

$$MnO_2 + H_2SO_4 + H_2O_2 = MnSO_4 + O_2 + 2H_2O$$

The volume of oxygen evolved can be measured and the manganese (IV) oxide can be calculated from the STP volume of oxygen (Vogel, 1961).

# EXPERIMENTAL

## i) Method Employed in the Determination of Manganese (IV)

### Principle:

Manganese (IV) was determined as $MnO_2$ (or pyrolusite) by treating samples with excess of acidified standard solution of arsenious oxide as a reducing agent. The excess of reducing agent was determined by titration with standard permanganate solution. $MnO_2$ present in the sample was calculated from equivalent amount of arsenious oxide consumed in the titration. (Vogel 1961).

$$2MnO_2 + 2H_3AsO_3 + 4H^+ = 2Mn(II) + 2H_3AsO_4 + 2H_2O$$

### Procedure:

The samples were dried at 120°C to constant weight. A small amount of sample (0.1000 g) was weighed in triplicate and transferred into 250 ml conical flasks. Standard 0.1N arsenious oxide solution and 10 ml of concentrated sulphuric acid were added. A short funnel was placed in the mouth of each flask and the samples were boiled until no black or brown particles were present. The solutions were cooled; 2 drops of 0.0024 M potassium iodide solution added and the excess of arsenious oxide was titrated with standard 0.098 N potassium permanganate. The

percentage of manganese (IV) was calculated from the equivalent amount of arsenious oxide consumed in the titration. A reference material containing known amounts of manganese dioxide was subjected to similar digestion procedure and was used as a confirmation of the analytical results.

ii) Method used in Determination of Manganese (III)

Principle:

Manganese (III) occurs in nature in minerals such as braunite $(Mn,Si)_2O_3$ and manganite $(Mn_2O_3nH_2O)$. The simple manganese (III) cation is extremely unstable in aqueous systems. In neutral solutions manganese (III) is reduced to manganese (II) even in the absence of reducing agents; in acid solutions it spontaneously disproportionates to manganese (II) and $MnO_2$ and in basic solutions manganese (III) hydrolyses to $Mn(OH)_3$ and is oxidized to $MnO_2$ by air (Cotton and Wilkinson, 1966). Hence a method for determination of manganese (III) in solution must attempt to stabilize the trivalent ion. Kolthoff and Watters (1943) have shown that manganese (III) can be stabilized by formation of pyrophosphate anionic complexes which are strong oxidants that can be titrated with a reducing agent. Hence the titrimetric mehtod proposed by Dolezal et al. (1963) was slightly modified and adopted for manganese (III) determination. Manganese (III) is reacted with dipotassium hydrogen phosphate in phosphoric acid media and reacted with excess standard potassium iodide

solution. The equivalent amount of iodide liberated was then titrated with standard thiosulphate solution in the presence of starch indicator.

Procedure:

An accurately weighed (1.000 g) portion of sample was thoroughly mixed with 2 g of dipotassium hydrogen phosphate (A.R.) and 15 ml of concentrated perchloric acid was added. The mixture was slowly heated to near dryness. Concentrated phosphoric acid (5 mls) and perchloric acid (5 mls) were added and the samples were heated to dryness. The cool residue was dissolved in phosphoric acid (20 mls). Potassium iodide 0.1N solution (50 mls) was added and the equivalent amount of iodide liberated was immediately titrated with standard thiosulphate in the presence of starch as indicator.

$$2Mn\ (III) + 2I^- = I_2 + 2Mn\ (II)$$

The amount of manganese (III) in sample was calculated from the equivalent amount of iodine liberated which was measured from the amount of thiosulphate consumed in the titration.

iii) Method for Determination of Manganese (II)

Principle:

The method used for determination of the manganese (II)

ion is based on the reaction between this cation and standard EDTA solutions. Manganese (II) EDTA complexes are colourless and are moderately stable in weakly acid solutions (Kolthoff et al., 1961). Because of the low stability constant of Manganese (II) EDTA complexes, it is difficult to titrate manganese (II) ion except in near neutral or alkaline media. However, manganese (II) complexes tend to precipitate as hydroxides in alkaline solutions (Mellor, 1932). Hence potassium sodium tartrate must be added to the solutions before neurtralizing. In addition, manganese (II) complexes tend to undergo oxidation in alkaline media and must always be titrated in the presence of a reducing agent such as ascorbic acid. Any transition metals in the sample solution may be masked using cyanide which does not form complexes with manganese

Procedure:

The method followed in the determination of manganese (II) cation was obtained from West (1969). A portion of the manganese sample (0.1000 g) was accurately weighed in triplicate and placed into 250 ml beakers and 10 ml of dilute nitric acid (1+3) and perchloric acid (10 ml) were added and the samples were heated till no black or brown particles were present. Distilled water (100 ml) and a small amount of ascorbic acid were added and the mixture was shaken until ascorbic acid dissolved and 5 ml of 20% potassium cyanide solution were added. Potassium sodium tartrate

(2 g) was added and the solutions were shaken. Solochrome Black T indicator was added and ammonia buffer was added till the pH of the solution was about 6. The solutions were titrated immediately using 0.1M EDTA solution to the red to blue end point. The concentrations of manganese (II) was determined from the amount of EDTA solution consumed.

Calculation:

1ml of 0.1M EDTA = 5.494 Mn (II)

## DISCUSSION OF RESULTS

The results obtained from these titrations were so variable and non-reproducible that they had to be rejected. Particular difficulties were encountered when dealing with samples having low total manganese to total iron ratios such as P5, NH1, NH2, and NH3. In addition the endpoint was frequently obscured by colour interferences from the sample solutions and , although the samples were gently warmed to improve detectibility of the end point it was still not possible to obtain adequately reproducible data. Consequently, it was decided that another method be used to see if more precise and reproducible data could be obtained.

Method for the Direct Titrimetric Determination of Manganese (II)

Procedure:

A method discussed by Malat et al. (1954) and Suk and Malat (1956) and outlined by Welcher (1958) was employed in the direct titrimetric determination of manganese (II). An aliquot of sample solution (10 ml) digested in perchloric acid as described earlier (see page 28 ) was placed into a conical flask and diluted with 50 ml of distilled water. A small amount of hydroxylamine hydrochloride was added to prevent oxidation of the manganese (II) ion. The pH was adjusted to about 6 using a buffer solution prepared by mixing equal volumes of 1M ammonium chloride and 1M ammonium hydroxide and 5 drops of 0.1 per cent aqueous solution of Pyrocatechol Violet indicator were added. The solutions were titrated immediately with standard 0.1 M EDTA solution to a colour change from greenish-blue to reddish purple. The concentration of manganese (II) in the sample was calculated from the equivalent amount of EDTA solution consumed in the titration.

1 ml of 0.1M EDTA = 5.494 mg of Mn (II)

## RESULTS

Once again the results obtained were non-reproducible and of poor quality and the concentration of manganese (II) in the samples was determined by difference by subtracting the sum of Mn (III) and Mn (IV) from total manganese obtained by flame atomic absorption spectrophotometry. The problem of determining manganese (II) in these samples is probably due to the low concentrations of Mn (II) and the presence of large amounts of iron.

## DISCUSSION OF RESULTS OF MANGANESE OXIDATION STATES

The analytical data for Mn (IV), Mn (III) and Mn (II) are given in Table 4. The data indicates that manganese (III) is the predominant oxidation state probably corresponding to the mineral braunite. Mn (IV) is the second most predominant oxidation state followed by Mn (II) which occurs in quantities less than 1% on average. Problems were encountered in determination of manganese (II) probably due to interference of the large amounts of iron present relative to the low occurrences of manganese (II). Two different titrimetric methods were used and in each case the data obtained was not satisfactory. Hence manganese (II) was determined by difference. In the case of Manganese (IV), a reference material containing known amounts of manganese dioxide (A.R.) was available and was analyzed in a similar manner as the samples. An average of 99.42% $MnO_2$ was obtained; 99.3% $MnO_2$ is the certified concentration of the reference material used.

TABLE 4: Analytical Data of Oxidation States of Manganese in New Brunswick Manganese Deposits.

| | % Mn (Iv) | % Mn (III) | % Mn (II) |
|---|---|---|---|
| NH 1 | 0.95 | 2.51 | 0.34 |
| NH 1 | 0.94 | 2.51 | 0.34 |
| NH 1 | 0.95 | 2.60 | 0.32 |
| NH 2 | 1.07 | 2.28 | 0.32 |
| NH 2 | 1.07 | 2.28 | 0.32 |
| NH 2 | 1.14 | 2.28 | 0.29 |
| NH 3 | 1.49 | 0.94 | 0.13 |
| NH 3 | 1.48 | 0.91 | 0.22 |
| NH 3 | 1.47 | 0.99 | 0.15 |
| P 1 | 2.36 | 4.79 | 0.21 |
| P 1 | 2.35 | 4.79 | 0.23 |
| P 1 | 2.34 | 4.84 | 0.20 |
| P 2 | 3.31 | 4.17 | 1.01 |
| P 2 | 3.30 | 4.17 | 0.97 |
| P 2 | 3.35 | 4.15 | 0.97 |
| P 3 | 2.50 | 3.88 | 0.68 |
| P 3 | 2.48 | 3.81 | 0.77 |
| P 3 | 2.37 | 3.88 | 0.81 |
| P 4 | 4.00 | 5.13 | 0.83 |
| P 4 | 4.06 | 5.36 | 0.56 |
| P 4 | 4.06 | 5.25 | 0.66 |
| P 5 | 0.12 | 0.25 | 0.09 |
| P 5 | 0.10 | 0.23 | 0.12 |
| P 5 | 0.11 | 0.27 | 0.09 |

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